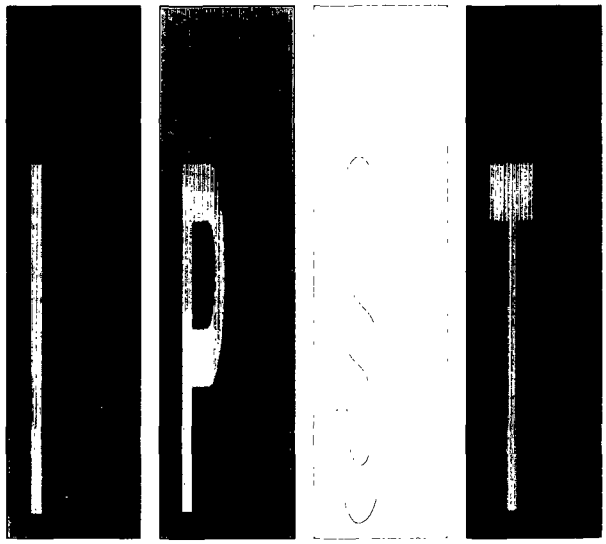
Institute of Paper Science and Technology

ANNUAL RESEARCH REVIEW

MECHANICAL PULPING

March 24, 1992



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INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

Atlanta, Georgia

ANNUAL RESEARCH REVIEW

MECHANICAL PULPING AND BLEACHING

MARCH 24, 1992

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PROJECT 3729

IMPROVED CHEMITHERMOMECHANICAL PULP

RESEARCH REVIEW

MARCH 24, 1992

Alan W. Rudie

Technical Program Review Report

PROJECT TITLE: Improved Chemithermomechanical Pulp

PROJECT STAFF: A. W. Rudie

BUDGET: $55,000

REPORTING PERIOD: March 1991 - March 1992

DIVISION: Chemical and Biological Sciences Division

PROJECT CODE: CHIPS

PROJECT NUMBER: 3729

OBJECTIVE:

Improve the performance of the chemithermomechanical pulping process.

GOAL:

An improved understanding of the performance limitations inherent in mechanical and chemithermomechanical pulping.

SUMMARY:

This project has evolved from a former project (Project 3566, High Strength, High Yield Pulps) which was dedicated toward minimizing fiber strength losses in the manufacture of high yield pulps and developing procedures to retain fiber strength. Project 3729 is more broadly defined to encompass greater participation in the Georgia Tech Center for High Yield Pulp Science (CHYPS). Due to a failure to secure sufficient Government and Industrial funding and a legal concern that has delayed the leasing agreement between Georgia Tech and the Georgia Power Corporation, activity at CHYPS has been limited during the year. The project has supported CHYPS in the preparation of a grant proposal and supporting documents for the U.S. Department of Energy.

The majority of the project work this year has focussed on a methods development for characterizing high yield pulps at very low energy input, well before the fiber is suitable for the preparation of handsheets. The chlorite holopulping process has been used to delignify the wood or fiber and prepare a chemical quality pulp while maintaining the remaining strength and integrity of the high yield fiber. In theory, the method will develop sufficient fiber bond strength to make fiber strength the limiting parameter in handsheet testing. Early evaluations of the method have focussed on quantifying fiber damage from chip compression in plug screw feeders.

The initial attempts with the chlorite delignification procedure encountered several problems. Poor chlorite penetration was addressed by using a vacuum impregnation process to insure good penetration of chlorite into the chips for the first two treatment stages. This also helped to reduce the number of treatments required. Filtration problems were attributed to a gel like film that develops during the extraction stages. Filtering the pulps on wire mesh screens after the final delignification steps has minimized this problem.

The chlorite method was tested on samples of southern pine wood chips crushed in a compression cell designed to be used in a hydraulic press. This experiment varied the temperature and compression ratio to induce a range of compression damage. After chlorite delignification, the fibers were characterized by handsheet testing, fiber length, and optical microscopy. A control chip sample and two samples of chips treated in the first stage plug screw feeder in the CHYPS pilot plant were also evaluated.

Several problems became apparent in this experiment. The control chips did not give the highest freeness pulp or highest strength handsheets. In addition, there was not a good correlation between treatment severity and pulp properties. A high test standard deviation indicated a problem with pulp uniformity and handling. With all these limitations, the results did give firm evidence of significant fiber damage in the pilot plant plug screw feeder. This was observed as a short fiber length, low freeness and low zero span tensile strength.

This experiment was then repeated with just two sets of pressing conditions, and the control sample of chips. In this case much greater care was taken to insure a uniform chip source and each set of chip pressing conditions was performed in triplicate. The control chips were sampled twice.

Screening the pulp before forming the handsheets has reduced the standard deviation for tests within a sample by 40%. Unfortunately, the range between replicates is still around 15% and the difference between the two treatment conditions averages only 5%. There is a 12% loss in zero span tensile index between the control chips, and the samples pressed in the compression cell. These differences are not statistically significant.

INTRODUCTION

Papers made from mechanical pulp are generally a fiber bonding limited structure.[1] However, for sulfite chemithermomechanical pulp[2] (CTMP) and alkaline peroxide chemimechanical pulps[3] (APMP) the tear index goes through a maximum with increasing specific energy and tensile index. This indicates that both pulps reach the point where bond strength exceeds fiber strength and the paper will benefit from improved processing to preserve the native strength of the wood fibers.

In trying to detect fiber strength losses in mechanical pulping, it is important to consider fiber damage that occurs early in the process. Fibers damaged in chipping, chip handling, chip compression in the plug screw feeders and in the initial size reduction in first stage refiner, all increase the susceptibility of the fiber to cleavage later in the process. Damage that occurs early in the process is generally not detectable in conventional processing. By the time pulp has been refined to a papermaking freeness it is nearly impossible to distinguish between damage that occurred early in the process and was aggravated by the refiners, from and damage caused exclusively by the refiners.

Several methods can be proposed to obtain information on native fiber strength and fiber damage occurring early in the mechanical pulp manufacturing process. Tensile testing on small wood sections will indicate damage but it may be difficult to distinguish damage to the fiber S_2 layer from rupture of the primary wall or S_1 layers, both of which will reduce the strength of the wood but have little effect on the strength of the fibers. Furthermore, testing small wood sections is not suitable throughout the refining process. Near the end of the process, relatively few large shives remain and an evaluation based on the strength of the remaining shives becomes influenced by structural characteristics that control the formation of shives such as ray crossings.

It is also possible to separate the fibers chemically and measure fiber strength with single fiber testing or by standard handsheet testing. Single fiber testing has the advantage that interfiber bond strength is not important and will not influence the results. It has the disadvantage of being tedious and requiring relatively long fibers or fiber fragments. Furthermore, variations in lignin and hemicellulose content between fibers will increase the variability and may become statistically confounded with fiber damage.

Handsheet testing has the advantage of using a fully representative sample of the wood (pulp) and can be readily adjusted for the average pulp yield from the chemical delignification process. It suffers the disadvantage that fiber bond strength, fiber strength and the presence of handsheet defects all influence handsheet strength. These problem can be minimized by relying on zero span[4] and short span[5] tensile testing as the primary measure of fiber strength. Handsheet defects such as shives and variations in basis weight will increase the standard deviation in the handsheet testing These can be controlled by proper preparation of the pulp for sheet forming.

Holopulping and handsheet testing have been selected for evaluation in this project. It is expected that successful development of this technique will enable us to investigate fiber damage occurring throughout the early stages of the mechanical and chemimechanical pulping processes and with proper attention to the role of the fines, can also offer useful information on fully refined pulps. Chlorite[6] and peracetic acid[7] holopulping provide a means to selectively delignify wood at any point in the wood handling and pulping process and will provide the basis for this study. Techniques developed here will be useful in the evaluation of any mechanical or chemimechanical pulping process. If successful, they will be applied to the sulfite CTMP projects proposed for CHYPS and the APMP process evaluation planned for fiscal year 92/93.

REVIEW OF PAST PROJECT ACTIVITIES

Project 3729 is a new project for the 91/92 fiscal year.

DISCUSSION OF 1991 RESULTS:

Due to the failure of CHYPS to secure funding and a limitation on work at the pilot plant because of problems in establishing Georgia Tech's lease on the site, there has been very little work with the pilot plant this year. The leasing arrangements between Georgia Tech and Georgia Power are nearly complete and we may see more activity at CHYPS next fiscal year.

Work on this project has focussed on two areas:

- Evaluation of the ability to model plug screw impregnation such as the Sunds Defibrator PREX® and the Sprout Bauer Impressafiner® by using a laboratory compression cell and a Carver hydraulic press. This is required to proceed with an alkaline peroxide mechanical pulping project.

- Evaluation of chlorite holopulping to delignify wood chips and destructured wood chips for zero span tensile analysis.

Evaluation of the Compression Cell:

A drawing and description of the use of the compression cell is given in the experimental section of the report. Results of the initial evaluation of the compression cell are summarized in table 1. For comparison, samples of the same wood chips were recovered from the first stage PREX® impregnator of the CHYPS pilot plant. These are listed at the end of table 1 as experiments 10 and 11.

Table 1. Initial chip impregnation experiments.

Run #	Compression Ratio	Temperature ° C	Expressed Water, %*	Absorbed Water, %
1	3 to 1	25	27.8	30.0
2	3 to 1	90	44.8	54.3
3	4 to 1	90	59.2	55.2
4	4 to 1	25	43.9	45.3
6	4 to 1	60	62.8	58.7
7	3.5 to 1	65	58.3	61.0
8	none, w/o water	90	0	6.7
9	none	90	0	39.9
10	-	25	?	44.0
11	-	90	?	105.9

Expressed water is % on OD wood. Absorbed water is expressed water +/- weight gain in the experiment. For the PREX® cases, absorbed water is determined from chip consistency entering the plug screw feeder, and chip consistency exiting the absorption tower. Expressed water is not accounted for.

A plug screw compression impregnation device is expected to give a liquor uptake around one kg of water per kg of wood[8]. The pilot plant PREX® impregnator has achieved this with a net increase in water content of 1.05 kg of water per kg of wood. It is unknown how much water was expressed in the compression stage of the PREX® system so the actual water absorbed by the expanding chips is actually somewhat higher. Unfortunately, none of the experiments in the compression cell have achieved target 1 to 1 ratio. The best result observed is experiment 7 with an estimated water absorption of 0.6 kg water per kg of wood.

A second series of experiments was conducted with the compression cell to evaluate the reproducibility of the system. In this experiment, all samples were pressed to the load limit of the press, 24,000 psi. The compression ratio was left as a dependant variable. Three separate samples were compressed at room temperature, and another three samples after 30 minutes of atmospheric steaming. This data is reported in table 2.

Table 2. Follow up chip impregnation experiments.

Run #	Temperature ° C	Compression Ratio	Expressed Water, %	Absorbed Water, %
1	25	3.5 to 1	8.9	57.9
2	25	3.6 to 1	9.2	57.1
3	25	3.6 to 1	10.0	57.2
4	100	3.8 to 1	44.8	102.7
5	100	4.0 to 1	50.5	112.6
6	100	3.8 to 1	43.4	95.7

281 OD grams of wood chips at 61% solids content. All chips compressed to 24,000 psi.

At 100° C the water absorption increases because steam formed in the lumens of the fibers condenses, drawing in additional water. The higher temperature also allows the chips to crush more easily, giving a higher compression ratio at maximum press load. In this case, at 100° C the chips have absorbed 1+ kg of water per kg of wood. At room temperature, the chips absorb around 50% of their dry weight in additional water, similar to the results reported in table 1.

The reproducibility of the results is acceptable with about a 15% variation in overall water absorption when the chips are heated to 100° C.

The ability to stabilize peroxide in the alkaline peroxide mechanical pulping process depends on getting complete penetration of the chips with the initial DTPA pretreatment, good removal of the solubilized metals, and good penetration of the stabilized peroxide solution. The water absorption at 100° C looks sufficient to meet these requirements. There is still the possibility that the shredding action of a commercial plug screw feeder and the resultant reduction in chip size will also be important to obtaining complete penetration of the chips. This is the next step in evaluating the lab compaction cell. In this experiment, chips will be treated with DTPA in the laboratory cell. The chips will then be steamed and pressed again to remove the filtrate and the soluble metals. Analysis of the original chips and the treated chips for transition metals, will indicate if the treatment is successful. In addition, a commercial sample of wood chips from a Bauer Impressafiner® will be evaluated in the same way to determine if the size reduction is important.

Chlorite Holopulping For Detecting Fiber Damage:

The chlorite holopulping process is reported in the experimental section. There are several key elements of the process that improve performance and handling for chips instead of thin wood

sections. A vacuum impregnation step improves the chlorite consumption and delignification efficiency of the first two chlorite treatment steps. After these two treatments, the fiber lumens are saturated and the partially delignified wood no longer degasses when place under a vacuum. Without the precautions to improve chemical penetration, the chips invariably delignify from the surface, leaving hard chip cores. It has also been observed that after the chips are broken up in the British Disintegrator, the alkaline extraction stages filter very poorly. This is attributed to a gel like substance that plugs the filter paper and retards filtration. A 150 mesh wire screen has been substituted for filter paper in this filtration step to avoid the delays experienced with paper filters. It is assumed there will be some pulp fines lost in this process but the fines do not make a significant contribution to zero span tensile and the fiber strength can be adjusted for the yield loss.

The wood chips compressed in the laboratory cell and reported in table 1 were holopulped with chlorite to determine if the compression caused any fiber damage. This data is reported in table 3. The run numbers reported in this table correspond to the numbers in table 1.

Table 3. Initial evaluation of chlorite holopulping.

Run #	Tensile Index Nm/g	Tear Index $mN \cdot m^2/g$	Zero Span Tensile Nm/g	Fiber Length mm	Damaged Fiber %	Freeness ml
C	135.9	12.2	311.2	3.34	43	590
1	133.7	12.1	278.1	3.32	47	640
2	131.1	11.7	314.2	3.32	52	640
3	132.4	12.4	331.6	3.37	49	660
4	140.0	12.4	361.6	3.29	60	650
6	137.3	12.6	325.2	3.35	60	630
7	130.4	12.9	340.2	3.40	66	620
8	122.8	13.6	314.4	3.24	66	630
9	122.3	14.3	380.8	3.28	58	600
10	141.8	11.8	267.3	2.94	97	510
11	142.6	12.4	274.5	2.78	97	560

Experimental conditions are from table 1. C is a control experiment conducted on the starting wood chips.

Since the control experiment with the original wood chips (Run C) has not produced the highest strength pulp as measured by tensile index, tear index or zero span tensile index, it is not clear how to interpret these results. In addition, experiments 8 and 9 are on a chip source that has

not been damaged by compression in the press. These should give similar results to the control experiment but instead show substantial differences. What is clear is that there has been measurable fiber damage induced in the pilot plant plug screw feeder (runs 10 and 11). This shows up as a lower tear index, zero span tensile index, a shorter average fiber length, and a lower freeness after holopulping. The increase in tensile index is to be expected if the plug screw feeder also increases the fiber surface area. This is confirmed by the lower freeness of these samples.

Since the source of the variation observed in table 3 was not clear, it was decided to repeat the experiments using replicate samples. Both the chip crushing step and the chlorite delignification step were repeated. The chip crushing data has already been reported in table 2. The results of the chlorite holopulp handsheet testing are reported in table 4.

Table 4. Replicate chip crushing and holopulping experiments.

Run #	Tensile Index N·m/g	Tear Index mN·m²/g	Zero Span Tensile N·m/g	Fiber Length mm	Scattering Coefficient m²/kg
Control 1	68.4	14.0	155.7	3.57	20.8
Control 2	70.9	12.7	152.4	3.54	21.4
1	60.8	12.1	142.7	3.64	20.0
2	65.0	13.5	120.2	3.44	20.4
4	55.1	11.7	139.6	3.40	18.9
5	73.1	13.9	144.5	3.40	21.4
6	69.6	14.0	123.3	3.56	21.5
1B	59.9	9.14	147.6	3.36	18.1
6B	78.7	10.2	130.6	3.29	18.1

Experiments are for chips crushed under the condition reported in table 2. Run 1B is the same chip source as run 1 but with the chlorite delignification conducted at 60° C. Run 6B is the same chip source as run 6 but with the chlorite delignification carried out at 60° C.

In this set of experiments, run 1 and 2 are replicates with the chip crushing conducted at 24,000 psi and room temperature. Runs 4,5 and 6 are replicates with the chip treatment at 24,000 psi and 100° C. Run 1B is an alternative chlorite treatment of run 1 and run 6B is the alternative chlorite treatment of run 6. This treatment is similar to the standard method except that the chlorite stages are conducted at an elevated temperature. In this set of experiments, all chips were from one log freshly chipped in the pilot plant chipper and screened on the Williams Classifier. Only chips less that 3/4" and greater than 1/2" were used to minimize the chip

variation between samples. The maximum range between replicates is 22 N·m/g (Runs 1 & 2) for Zero Span Tensile Index, and 18 N·m/g (Runs 4 and 5) for Tensile Index. These correspond to about a 17% variation in Zero Span and 27% variation in Tensile Index. This confirms the level of variation observed in the first set of experiments. On average, the controls exceed both sets of crushed chips in Tensile Index, Tear Index and Zero Span Tensile Index. On average, the chips crushed at 100° C have higher strengths than the chips crushed at room temperature. On average, the alternative chlorite treatment gives lower tear index and scattering coefficient. Given the large variation observed in replicate experiments, none of these differences is statistically significant.

Experimental Procedures

Laboratory Impregnation Cell

A drawing of the laboratory impregnation cell is given in figure 1. To impregnate chips in the laboratory cell, the screen cylinder (item 5) is placed inside the immersion vessel (item 8). The handles on the cylinder are aligned with slots in the sides of the immersion vessel to allow the cylinder to sit on the bottom of the vessel over the bottom plate (item 9). The screen cylinder is loaded with 250 - 300 g OD wood chips. Chips can be heated by pushing a flexible, low pressure steam line through the wood chips to the bottom of the cylinder and steaming for the desired length of time. The impregnator is shaken to compact the chips and the ram (item 1) placed on the chip mass and a measurement taken from a scale on the side of the ram to determine the initial chip volume. The Impregnator is then placed in the press and compressed to the desired final volume again using the scale on the side of the ram. A 3 inch spacer is available to complete the compaction when the desired volume reduction exceeds the cylinder travel of the press. After completing the compaction, the immersion vessel is drained of any expressed filtrate and filled with the solution to be added to the chips. The press pressure is released and the screen cylinder raised and turned so that the handles sit on the top rim of the immersion vessel. Generally, the majority of the chip plug will remain compacted in the screen cylinder. The plug can then be forced out of the screen cylinder into the bottom of the immersion vessel by applying pressure to the ram.

Where temperatures below 100° C are listed in the text, the temperature was raised 5° above the target temperature and the pressing started when the temperature had fallen to the desired temperature. The experiments listed in table 2 were carried out by presteaming the wood chips for 30 minutes under atmospheric conditions.

Chlorite Holopulping

For these experiments, a stock buffered chlorite solution is prepared as follows: To a 1 liter volumetric flask, add approximately 500 ml of distilled water, 60 g (0.66 moles) of reagent grade sodium chlorite and 60 g (0.72 moles) of reagent grade sodium acetate. Dilute to the

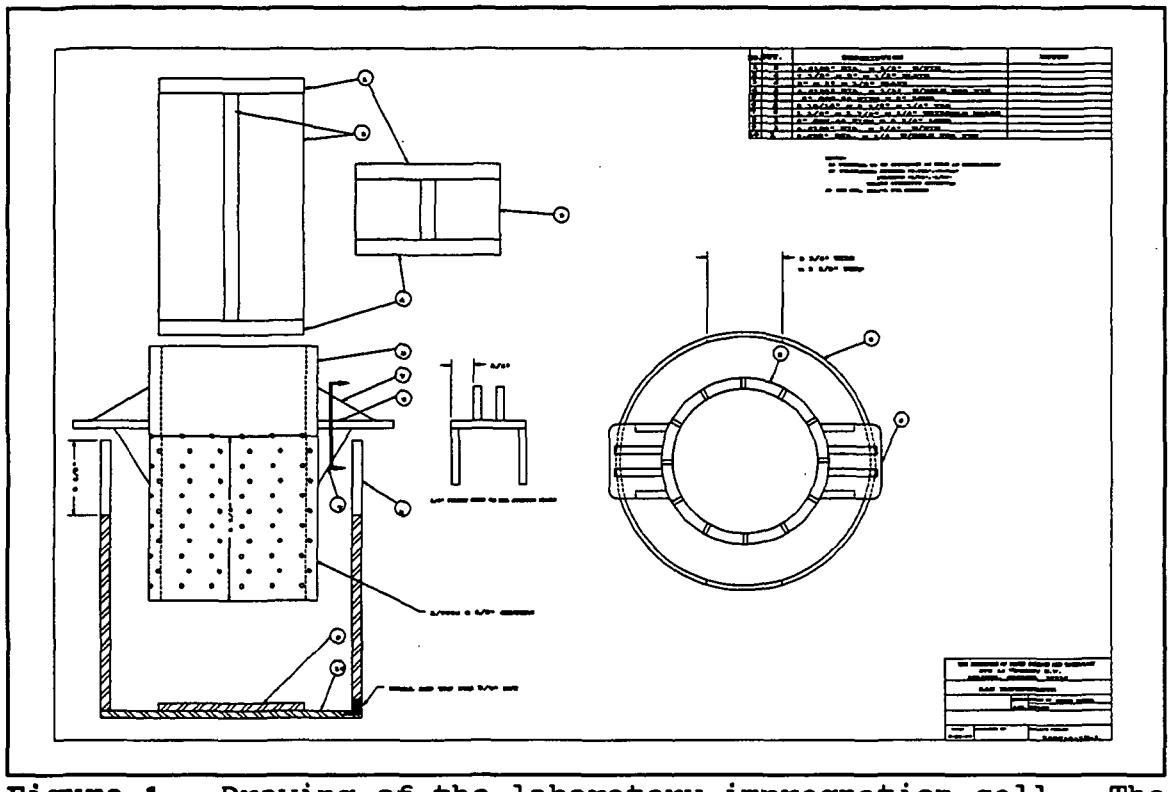

Figure 1. Drawing of the laboratory impregnation cell. The cell capacity is 250 OD grams of wood chips with a maximum compression ratio of ≈ 5 to 1.

mark with distilled water. This reagent is photosensitive but is otherwise stable and can be stored for several months if kept in the dark.

To delignify wood chips, place 50 g (OD basis) wood chips in a 500 ml Erlenmeyer flask. Add 300 ml of buffered sodium chlorite solution and 20 ml of reagent grade glacial acetic acid. Attach the flask to a vacuum source and evacuate for five minutes. Turn off the vacuum source and slowly allow air into the flask. Place the flask under vacuum for another five minutes and release the vacuum to air again. Stopper the flask and place in a dark cabinet underneath a fume hood. After 30 minute to 1 hour, a distinct yellow green color should be observed indicating that chlorine dioxide is forming in the flask. At room temperature the wood chips will take 4 to 5 days to consume the majority of the chlorite. The sodium acetate buffer will maintain the pH around 4 for the entire course of the reaction. Once the majority of the sodium chlorite/chlorine dioxide is consumed, filter the wood chips and wash once with distilled water. Transfer the chips back into the Erlenmeyer flask and add sufficient distilled water to cover the chips. Let the wood soak in the distilled water over night and filter again or decant the wash water. Add 200 ml of 0.15 N NaOH, cover the Erlenmeyer flask and let the wood soak for 24 hours. Filter or decant the alkaline solution and check the pH. If below 9.0 repeat the caustic extraction by adding another 200 ml of 0.15 N NaOH and letting the chips soak another 12 to

24 hours. Filter and wash the chips thoroughly. Place them back into the Erlenmeyer flask and repeat the chlorite procedure as described above with the exception of using 200 ml of chlorite stock solution and 20 ml of acetic acid.

The second chlorite procedure is followed by a second caustic extraction. At this point the chips were broken up in the British Disintegrator (3000 revolutions). A third chlorite treatment is performed using 200 ml of stock chlorite solution and 20 ml of acetic acid. Since the wood chips are saturated, the vacuum step is ineffective and can be skipped. Follow the chlorite treatment with a final caustic extraction, wash and disintegration for 3000 revolutions in the British Disintegrator. This will render most of the remaining chips to shives and fiber. A final chlorite treatment is performed to complete the pulping process. The pulp is then washed thoroughly, disintegrated another 3000 revolutions and dewatered on a Büchner funnel.

Samples 1B and 6B were treated using an alternative chlorite procedure. In this case, after vacuum impregnation, the samples were placed in a hot water bath at 60° C for 8 hours. They were then allowed to sit at room temperature for an additional 12 to 36 hours before filtering and treating with caustic. All four chlorite steps followed this procedure.

Samples were tested for Viscosity (TAPPI T-230), Kajaani fiber length (reported as weight weighted average) and Freeness (TAPPI T-227). Handsheets were prepared according to TAPPI T-205 and tested for tensile index, tear index, scattering coefficient and absorption coefficient according to TAPPI 220. Zero span tensile index was carried out according to TAPPI T-231. Pulp viscosity was above 30 mPa·sec for all samples except the samples treated using the alternative chlorite procedure. These samples gave CED viscosities of 17.5 mPa·sec for 1B and 16.9 mPa·sec for 6B.

CONCLUSIONS AND RECOMMENDATIONS

The operation of the chip compression cell is marginal for accomplishing the displacement of entrained water required to proceed with the APMP part of the project. The efficiency at removing trace transition metals such as Manganese needs to be checked before proceeding into the APMP stage. This will be evaluated on both standard wood chips and a chip source already compressed once in a commercial plug screw feeder or the CHYPS pilot plant. If a larger displacement of transition metals is possible with the previously crushed chips, they will be used in the APMP work.

The large variation in the replicate chlorite holopulping experiments is disappointing. Since the three sets of undamaged wood chips from the first set of experiments show considerable sample to sample variation, it is suspected that the variation is occurring in the holopulping step. This can be evaluated by performing replicate experiments on a single source of wood chips. Unfortunately, we have been unable to obtain a usable pulp yield in either of the first two sets of holopulping experiments and this is considered crucial to fully understanding the process. This will be a priority in the next set of experiments. With the current precision, the process

can barely discern the fiber damage occurring in the CHYPS pilot plant plug screw feeders. Because of the small size of these units, it is suspected that they induce more fiber damage than a commercial plug screw feeder. If this is the case, the chlorite holopulping process will not be able to determine the extent of fiber damage in the commercial systems. An investigation of chips from a commercial system is planned for the next phase of this study.

FUTURE ACTIVITY

We expect to complete the chemical impregnation phase of this study this fiscal year or early next fiscal year. If we are able to resolve the remaining issues with the compression cell and the holopulping process, the project will proceed into the alkaline peroxide mechanical pulping phase of the project. This will evaluate the number of pretreatment stages required to obtain reproducible results[3,9], the peroxide and alkali charge required to optimize strength gains and minimize fiber damage, the extent of refining to be carried out in the first stage refiners and the effect of interstage washing before second stage refining. It is planned to investigate the process on both a hardwood (aspen or cottonwood) and the southern pines in the 92/93 fiscal year.

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PROJECT 3524

FUNDAMENTALS OF BRIGHTNESS STABILITY

RESEARCH REVIEW

MARCH 24, 1992

Arthur J. Ragauskas

TECHNICAL PROGRAM REVIEW FORM

PROJECT TITLE: FUNDAMENTALS OF BRIGHTNESS STABILITY

PROJECT STAFF: A.J. Ragauskas

BUDGET (FY 91-92): $115,000

REPORTING PERIOD: April 1991 - February 1992

DIVISION: Chemical and Biological Sciences

PROJECT NUMBER: 3524

OBJECTIVE: Research activities are directed at investigating the fundamental chemical reactions which are initiated when high yield-pulps are photolyzed. As our knowledge of the photoxidation of mechanical pulp increases, methods to stop or significantly retard the yellowing process will be pursued.

IPST GOAL: Increase the usefulness of high-yield fibers.

SUMMARY:

Advancements in the manufacturing and bleaching of high-yield mechanical pulps has resulted in the commercial preparation of pulps that have Tappi brightness levels of above 80%. To date, these pulps are used as furnishes for low-value or short-life paper products due to their tendency to undergo light-induced yellowing. It has been suggested that if the rate of brightness reversion was reduced from three to thirty six months, the potential market for bleached CTMP would be expanded by 0.6 to 2.2 million tonnes per year.

Clearly there is an increasing need to investigate the fundamental chemical reactions which are initiated when high-yield pulps are photolyzed and to apply this knowledge to halt or significantly retard the yellowing process. To accomplish this goal, research efforts have been focused on three important aspects of the brightness reversion phenomenon: the design of novel photostabilization techniques and reagents, the photo-formation of chromophoric structures, and the photo-reactivity of chromophoric structures.

Based upon the fundamental principal that brightness reversion of mechanical pulp is a photo-initiated oxidation of lignin, research efforts have been directed at examining the effectiveness of reagents which could be oxidized at rates comparable to lignin and yet remain colorless. Through an extensive survey of compounds, we have discovered three new structurally related sets of compounds which could retard relative rates of brightness reversion. All three sets of compounds are structurally related diene systems. The most successful reagent studied to date is trans,trans-2,4-hexadien-1-ol. Photo-reversion studies with BCTMP pulp samples treated with this alcohol have shown that this compound can photo-stabilize mechanical pulp as effectively as ascorbic acid. Although the application of this reagent has been shown to accelerate thermal reversion, several preliminary studies have suggested that this phenomenon can be halted.

The chemical mechanisms contributing to the photo-formation of chromophoric structures in mechanical pulp has also been explored in this research program. Research efforts over the past years have demonstrated that brightness reversion is initiated by the absorption of a photon of light by conjugated lignin structures. The excited state of these molecules then ultimately leads to the formation of radicals and the oxidation of lignin to highly colored material. The presence of α-carbonyl groups in lignin has been frequently cited as a principle component contributing to the formation of colored quinone-like structures in photo-yellowed mechanical pulp. The photo-reactivity of model lignin-like compounds has been studied by several groups and is believed to be a valid model for brightness reversion. Research efforts described in this report clearly demonstrate that current lignin model compounds employed in the literature fail to yield *ortho*-quinone like structures. Since *ortho*-quinones have been detected in mechanical pulp these results indicate that the exact chemical mechanisms involved in oxidizing phenolic structures in lignin to quinones is far from understood.

Finally, the photo-reactivity of chromophoric structures commonly believed to contribute to yellowing have also been studied. Employing a series of *para*- and *ortho*-quinone structures, we have determined that most quinone structures do not contribute to further photochemical yellowing of mechanical pulp. Research efforts have also demonstrated that hydroxy-*para*-quinones exhibit chemical behavior analogous to that of *ortho*-quinones. These results have important implications in the characterization of quinone structures found in mechanical pulp.

Photo-Stabilization of Mechanical Pulp

Introduction

Advances in mechanical pulping and bleaching have provided the means of manufacturing ultra high-yield pulps that have a Tappi brightness above 80%. At these levels of brightness, mechanical pulps could potentially be employed in high value paper products such as business forms, reprographic papers, and writing papers. However, the rapid light-induced yellowing of these brightened pulps restricts their use to short-life, low-value paper products. It has been suggested that if the relative rate of light-induced yellowing could be reduced from three months to thirty six months then the potential market for bleached CTMP would increase fourfold[1].

The principle component of mechanical pulps which contributes to photo-yellowing has been shown to be the lignin portion of the pulp. Although the photo-oxidation mechanisms have not been fully elucidated, significance advances have been made in understanding brightness reversion. It is now well recognized that extended conjugated structures present in lignin absorb near-UV light (λ=300-400 nm) and that the excited state of these structures leads to the formation of radicals[2]. Regardless of the exact mechanism responsible for generating the proposed radicals, it is generally accepted that these intermediates lead to the oxidative formation of *ortho*- and *para*-quinones. The presence of quinoid-like structures in photo-aged mechanical pulp has been detected spectroscopically[3], and these structures are believed to be one of the principle components contributing to the yellowing of mechanical pulp. Clearly then, photo-stabilization of mechanical pulp requires that the photo-initiated oxidation of lignin be halted.

Research efforts over the past 45 years have identified three general methods by which mechanical pulps can be photo-stabilized. High-yield pulps can be stabilized by reducing the lignin chromophores with sodium borohydride followed by an alkylation. This two-step process removes most lignin chromophores and stabilizes the pulp with respect to photo-oxidation of phenolic groups[4]. Alternatively, mechanical pulps can be stabilized with the addition of near-UV absorbing compounds such as dihydroxy or tetrahydroxybenzophenone[5]. These latter reagents absorb harmful near-UV light and convert it to thermal energy thereby halting the photo-initiated oxidation of lignin. Although both of these processes are effective, the costs associated with these technologies has prevented their implementation.

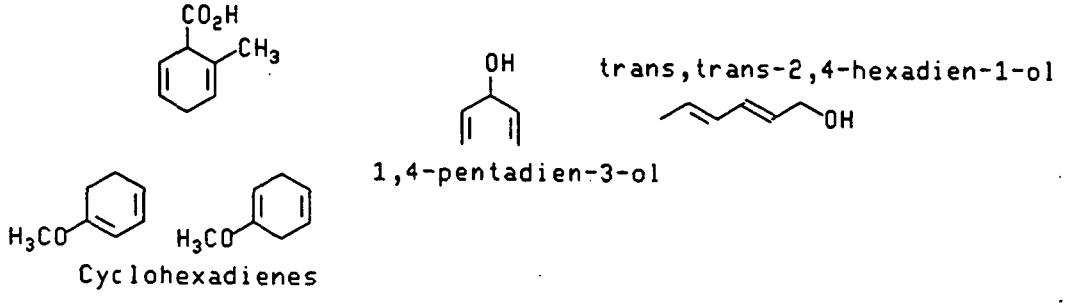
A more-promising approach to stabilizing mechanical pulp has been to design inhibitors which are oxidized at rates greater than that of lignin itself. Early research efforts of Janson and Forsskahl demonstrated the efficiency of several mercaptans to retard brightness reversion of high-yield pulps[6]. These observations have been further pursued by Sarkanen[7] and Daneault[8]. The results of their studies demonstrated that

reagents such as thiogylcerol and 1-dodecanethiol can substantially improve the photo-stability of mechanical pulps. The use of ascorbic acid as an inhibitor of light reversion has also been explored. The effectiveness of this reagent and the proposed mechanism of photo-stabilization has been investigated by Heitner and others[9].

Discussions of 1991 Results

Based upon the results of these inhibitor studies and other reports, we initiated a survey study to identify novel methods of retarding brightness reversion. The three types of reagents considered in this study can be classified into one of three categories, novel alkylating reagents, reductive treatments, and antioxidant reagents. To date, the most successful results have been found from the latter category. Table 1 summarizes the types of alkylating reagents and reductive treatments which were examined and shown not to have a positive effect on reducing the rates photo-yellowing.

In contrast to these results a series of three new structurally related sets of compounds have been discovered which have been shown to reduce the relative rate of brightness reversion. As shown below, we have found that substituted cyclohexadienes; 1,4-pentadien-3-ol; and trans,trans-2,4-hexadien-1-ol are all effective at retarding brightness reversion of BCTMP pulp samples.



Before examining the results of these studies, it is necessary to review the general experimental procedures employed and the means of reporting the photo-stabilization values. The experimental approach employed in our studies was to prepare a series of optical handsheets following Tappi procedures and then to wash these handsheets with methanol. The methanol wash was required to remove any extractives. Removal of the extractives was required so as to accurately determine the amounts of proposed inhibitor applied. A review of the literature[10] indicates that extractives do not contribute to photo-yellowing of mechanical pulp, and their absence in these experiments does not invalidate

the results. The handsheets were then air and vacuum dried; initial brightness values were recorded, and the pulp samples were then soaked in a methanolic solution containing the proposed inhibitor. After drying, the amounts of applied stabilizer were determined, and brightness values were measured. The photolysis experiments were preformed in either a Rayonet photochemical reactor with RPR-3500A lamps (λ=300-400) or with the Oriel solar simulator. All photolysis experiments were carried out in the presence of a second set of reference handsheets which had been methanol washed but not treated with the proposed photo-yellowing inhibitor.

The rate of yellowing was monitored by measuring the changes in brightness. To evaluate the effect of a given reagent on stabilizing mechanical pulp, we have employed the % stabilization concept developed by Lamont[11] (equation 1).

$$\% \text{ Stabilization (PS)} = 100\% * [(\Delta \text{ Brightness of treated sample} - \Delta \text{ Brightness of reference sample}) / \Delta \text{ Brightness of reference sample})]$$

Eq. 1

Our initial attempts at photo-stabilization of mechanical pulp employed 1-methoxy-1,3-cyclohexadiene (1,3-CHD); 1-methoxy-1,4-cyclohexadiene (1,4-CHD); and 1,2,4,5-tetramethyl-1,4-cyclohexadiene (TMCHD). Preliminary studies with 1,4-CHD indicated that the % stabilization was dependent upon the solvent the reagent was dissolved in. For example, handsheets treated with a solution of 1,4-CHD and dichloromethane yielded a negligible stabilization effect. Through a series of experiments with 1,4-CHD, it was determined that methanol was the best solvent to be employed. The stabilization effect for 1,4-CHD was also shown to be dependent upon the time of application. For example, handsheets treated with a 0.7 N 1,4-CHD/methanol solution for 15 min exhibited a maximum PS of 9%. In contrast, handsheets treated with methanolic 1,4-CHD for 2 h yielded a maximum PS of 21%. Based strictly upon experimental convenience, all handsheets were treated with methanolic solutions for 15 min.

Upon completing these preliminary experiments, research efforts were then focused on determining the efficiency of photo-stabilizing handsheets of TMP with 1,3-CHD; 1,4-CHD; and TMCHD. The results of these studies are summarized in Table 2, and the data clearly indicate that 1,3-CHD and 1,4-CHD can reduce the rate of brightness reversion. These studies were then repeated employing BCTMP hardwood pulp handsheets which had an ISO brightness of above 80%. The results of the photo-stabilization studies are tabulated in Table 2, and they demonstrate that the use of 1,3-CHD or 1,4-CHD can retard the relative rate of brightness reversion for low- and high-brightness pulps. The inefficiency of TMCHD to stabilize mechanical pulp was tentatively attributed to the hydrophilic nature of the molecule.

Although these results were promising, the use of 1-methoxy-1,3-cyclohexadiene or 1-methoxy-1,4-cyclohexadiene was difficult to study due to the volatility of these structures. The loss of inhibitor during reversion made studying the kinetics of this process virtually impossible. In an attempt to address these issues, handsheets of BCTMP were treated with 1,4-dihydro-2-methylbenzoic acid. It was anticipated that the carboxylate would prevent volatilization of the inhibitor and enhance the binding to the fibers. Furthermore, 1,4-dihydro-2-methylbenzoic acid retains the cyclic diene structure and so should act as a photo-stabilization reagent. Employing the usual experimental procedures doped handsheets were prepared and irradiated in the Solar Simulator. The results of these studies are summarized in Table 3, and the data indicate that 1,4-dihydro-2-methylbenzoic acid is a moderately effective stabilizing reagent. In comparison to the stabilization effects noted with 1-methoxy-1,4-cyclohexadiene the 1 and 2 h effects are comparable, but after 4 h of irradiation, the 1,4-dihydro-2-methylbenzoic acid treated handsheet continued to have a significant stabilization effect. The differences in stabilization were tentatively attributed to the differences in volatility of the compounds.

To investigate the possibility that the effectiveness of the above reagents was due to the conjugated olefinic ring structure, we surveyed a series of unsaturated cyclic compounds as potential photo-yellowing inhibitors. The potential use of 1,3-cycloheptadiene; cycloheptatriene; 1,3,5,7-cyclooctatetraene; abietic acid; 2-furoic acid; furfuryl; 2-thiophenecarboxylic acid; and 2-thiophenemethanol as photo-stabilization reagents was shown to be ineffective. Although these studies failed to identify alternative structural units which could stabilize mechanical pulp, they did contribute to our fundamental understanding of how the cyclic diene structures photo-stabilize high-yield pulps.

To determine if the photo-stabilization effect of 1,4-dihydro-2-methylbenzoic acid was due to its cyclic structure, we examined the stabilization effects for trans,trans-2,4-hexadienoic acid. This compound has been reported to be a "mild" photo-yellowing inhibitor[12]. The % stabilization effects for trans,trans-2,4-hexadienoic acid applied to BCTMP handsheets are summarized in Table 3. Although it is difficult to compare the differences in stabilization between the cyclic and acyclic inhibitor due to the differences in the level of application, it was interesting to note such a strong stabilization effect for the acyclic compound.

The photo-stabilization effect of trans,trans-2,4-hexadienoic acid promoted our interest, and we initiated a study to determine what structural components of this compound were needed for photo-stabilization. Preliminary studies indicated that both acrylic and crotonic acid were ineffective at stabilizing BCTMP handsheets. Based upon these results, we concluded that both double bonds needed to be present in the inhibitor to retard brightness reversion. Furthermore, it was shown that the sodium salt of trans,trans-2,4-hexadienoic actually accelerated brightness reversion. Based upon these results the photo-stabilization effects of trans,trans-2,4-hexadien-1-ol and hexadienal were investigated. As anticipated BCTMP handsheets treated with the aldehyde yellowed

rapidly, as summarized in Table 3. It was therefore much to our surprise the alcohol was shown to be a very effective photo-stabilization compound, as reported in Table 3.

Due to the significant photo-stabilization effects of trans,trans-2,4-hexadien-1-ol on BCTMP, this reagent was further investigated. Photolysis of treated handsheets for prolonged periods of time indicated a continuing stabilization effect, as summarized in Table 4. A comparison of the % stabilization effect for 2,4-hexadien-1-ol with ascorbic acid indicated that both reagents were near equal in their ability to retard photo-yellowing. The application of ascorbic acid and 2,4-hexadien-1-ol onto BCTMP handsheets yielded a mild synergistic effect. In conclusion these results suggest that hexadien-1-ol is nearly as effective a photo-stabilization reagent as ascorbic acid.

The physical and chemical changes occurring with BCTMP handsheets treated with hexadien-1-ol were also investigated. Scattering coefficients for the treated and untreated handsheets were determined before and after photolysis, and these data indicated no differences within experimental error. Likewise, it was established that the opacity of all of the handsheets remained constant. These results clearly suggest that the changes in brightness reversion are due to differences in the relative rates of chromophore formation in the treated and untreated handsheets. The diffuse reflectance spectrum (λ = 400 - 700) for the treated and untreated BCTMP handsheets was recorded at 0, 1, 2, and 4 h of irradiation. These spectra, shown in Figure 1 serve to illustrate the pronounced effect that trans,trans-2,4-hexadien-1-ol has on the photo-yellowing of the handsheets. Although all treated and untreated handsheets have the same initial spectrum, after 1 h of irradiation, the treated handsheets exhibit higher % reflectance than the untreated handsheets. This trend is then continued throughout the photolysis experiment.

The successful commercial implementation of a photo-stabilization reagent for BCTMP and other ultra high-yield mechanical pulps is dependent upon several crucial issues, including cost, safety, and thermal stability of the reagent. The latter condition has imposed a serious challenge to the application of hexadien-1-ol for inhibition of photo-yellowing. A series of long-term experiments just recently completed have indicated that the unsaturated alcohol accelerates thermal reversion (see Table 5). It is our opinion that the thermal reversion process takes place due to a slow autoxidation of hexadien-1-ol to hexadienal. This aldehyde is known to have an "off-yellow" color, and its formation could readily lead to an apparent thermal reversion of the treated pulp samples. Currently, we are attempting to develop novel methods of halting this process. Preliminary data in Table 5 indicate that BCTMP handsheets treated with a mixture of ascorbic acid and hexadien-1-ol do not readily undergo thermal reversion. These experiments are long-term in nature and will require several additional months to confirm these initial trends.

An alternative means of halting the thermal reversion process is to chemically alter the hexadien-1-ol structure so that autoxidation can not readily occur. The principle method we are pursing in this field is to convert the alcohol into an ether or ester functional group. Clearly, for such an approach to be feasible the alcohol functional group must not be

involved in the chemical processes contributing to photo-stabilization. Recent reversion studies with the acetate of hexadien-1-ol have demonstrated that the acetate is an effective stabilization reagent, and thermal reversion studies have been initiated.

Finally, we have examined 1,4-pentadien-3-ol as a photo-stabilization reagent for BCTMP, and moderate stabilizing effects were noted (see Table 4). Presumably, this compound reduces reversion in much the same manner as the cyclohexadiene structures, by donating a hydrogen atom to phenoxy radicals generated during brightness reversion.

Conclusions and Recommendations

In summary, we have discovered several novel reagents which could retard brightness reversion. Based upon the results of these studies and the literature we believe that the use of inhibitors to stabilize mechanical pulp has great potential and is not fully developed. The thermal reversion issues associated with trans,trans-2,4-hexadien-1-ol need be resolved for future success of this reagent and we are optimistic that this hurdle will be overcome.

Finally, these studies have discovered a new set of structurally related compounds which are effective at retarding brightness reversion. It is our goal to pursue these findings so as to develop new and effective methods of stabilizing mechanical pulp.

Future Activity

Future research efforts will focus on investigating methods of retarding thermal reversion of BCTMP samples treated with trans,trans-2,4-hexadien-1-ol. Several structural variations of hexadienol will be investigated to optimize both thermal and photo-stabilization effects. Alternative methods of applying trans,trans-2,4-hexadien-1-ol and other inhibitors onto BCTMP pulp samples will be evaluated. The effectiveness of these reagents with conventional lighting sources such as, natural sunlight, photocopiers, and office fluorescent lamps will be examined.

Future advances in photo-stabilization of high-yield pulps with the reagents developed in our laboratories requires a rigorous understanding of the fundamental chemical processes that contribute to their efficiency. It is anticipated that as we develop a refined understanding of the chemical mechanisms contributing to photo-stabilization we will be able to optimize inhibition of photo-yellowing. Future research efforts in this are directed towards studying the chemical fate and reaction mechanisms of the inhibitors discovered in this program. All studies will executed with BCTMP pulp samples and the results should impact directly on retarding brightness reversion in mechanical pulp.

Finally, we plan to continue pursuing our survey study of novel brightness reversion stabilization techniques.

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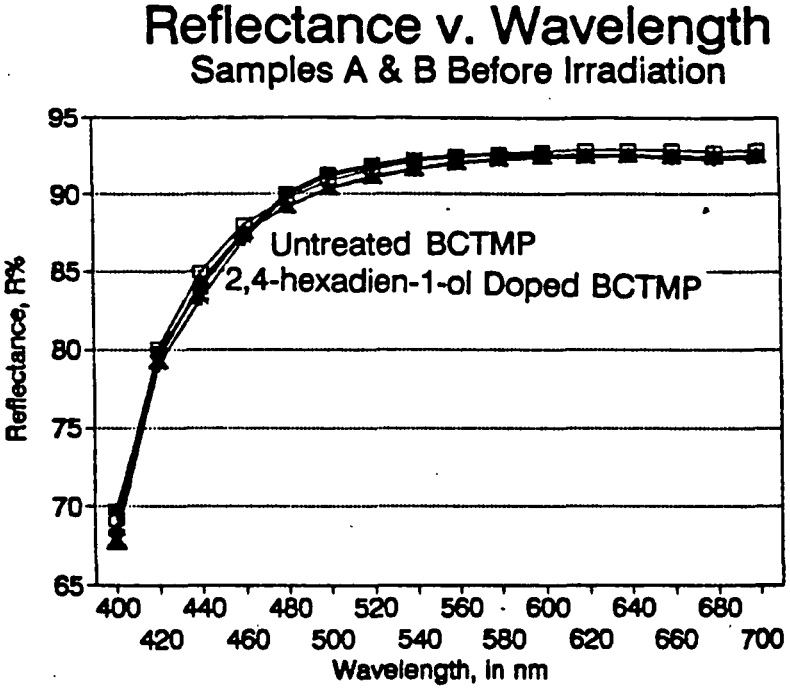
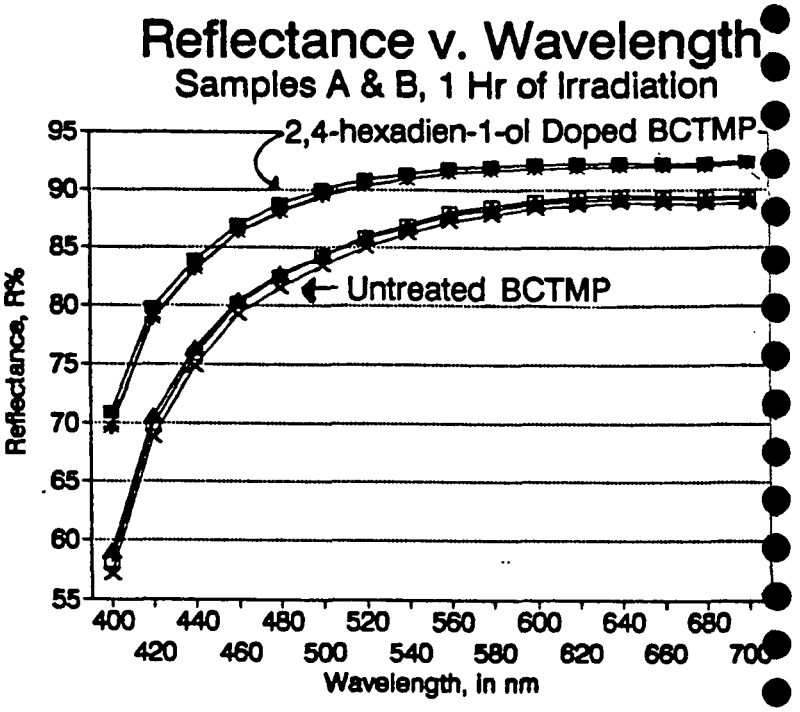
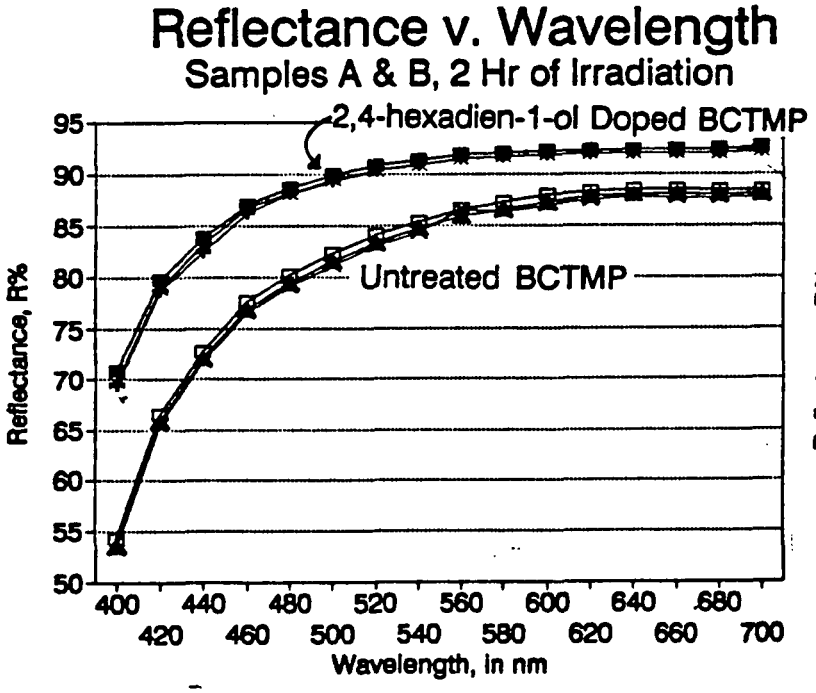






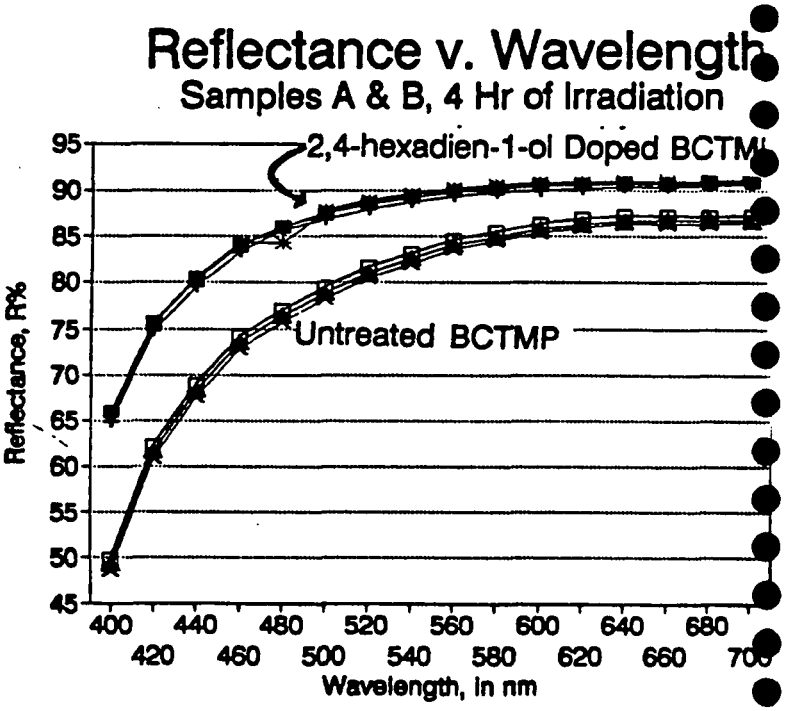


Figure 1 Diffuse Reflectance Spectroscopy of Untreated BCTMP Handsheets and trans,trans-2,4-hexadien-1-ol Doped BCTMP Handsheets

Table 1 List of Reagents Which Were Shown to be Ineffective at Stabilizing Mechanical Pulp

Phenoxy Blocking Reagents	Oxidizing Reagents
Phenyl Isocynate	Dimethyl Dioxirane
Ethyl Isocynate	
Dimethyl Acetylenedicarboxylate	Reducing Reagents
Thionyl Chloride	
	Zn/Acetic Acid/ Ultrasound

Table 2 Photo-Stabilization Effects for Mechanical Pulp Handsheets[a] Treated with Methanolic Solutions[b] of 1-methoxy-1,3-cyclohexadiene (1,3-CHD); 1-methoxy-1,4-cyclohexadiene (1,4-CHD); and 1,2,4,5-tetra-methyl-1,4-cyclohexadiene (TMCHD).

	% Stabilization[c]					
Period of Irradiation[d]/h	1,3-CHD		1,4-CHD		TMCHD	
	TMP[e]	BCTMP[f]	TMP	BCTMP	TMP	BCTMP
1	32	24	35	31	5	3
2	20	22	18	28	-5	2
4	3	7	-2	16	-3	2
Initial Brightness for Treated Handsheet[g]	60.4	84.4	58.7	87.8	56.8	85.9
Mass of Inhibitor Applied (g/g handsheet)	0.052	0.035	0.054	0.037	0.065	0.018

[a]optical handsheets were prepared from a commercial BCTMP hardwood pulp following standard Tappi procedures; [b]handsheets were soaked in a 10% by weight cyclohexadiene / methanol solution for 1/4 h and then air and high vacuum dried; [c]see equation 1 for a definition of % stabilization; [d]accelerated photo-aging was preformed with a Oriel Solar Simulator and all experiments were preformed in triplicate; [e]TMP was prepared from juvenile pine; [f] BCTMP was prepared from hardwood; [g] ISO Brightness

Table 3 Photo-Stabilization Effects for BCTMP Handsheets[a] Treated with Methanolic Solutions[b] of 1,4-dihydro-2-methylbenzoic acid (1,4-DHBA); trans,trans-2,4-hexadienoic acid (2,4-HDA); trans,trans-2,4-hexadienal (2,4-HDal); and trans,trans-2,4-hexadien-l-ol (2,4-HDol)

	% Stabilization[c]				
Period of Irradiation[d]/h	1,4-DHBA BCTMP[e]	2,4-HDA BCTMP	2,4-HDal BCTMP	2,4-HDol BCTMP	2,4-HDal BCTMP
1	27	40	-27	60	88
2	25	42	0	54	78
4	23	44	4	46	75
Initial Brightness for Treated Handsheet[f]	86	86.8	78	87.6	87.7
Mass of Inhibitor applied (g/g handsheet)	0.021	0.16	0.04	0.05	0.04

[a]optical handsheets were prepared from a commercial BCTMP hardwood pulp following standard Tappi procedures; [b]handsheets were soaked in a methanolic solution for 1/4 h and then air and high vacuum dried; [c]see equation 1 for a definition of % stabilization; [d]accelerated photo-aging was preformed with a Oriel Solar Simulator and all experiments were preformed in triplicate; [e]BCTMP was prepared from hardwood; [f]Tappi and ISO Brightness measurements.

Table 4 Photo-Stabilization Effects for BCTMP Handsheets[a] Treated with Methanolic Solutions[b] of trans,trans-2,4-hexadien-1-ol (2,4-HDol); Ascorbic Acid (AA); trans,trans-2,4-hexadienal (2,4-HDal); 1,4-pentadien-3-ol (1,4-PD); and the Acetate of trans,trans-2,4-hexadien-1-ol (A2,4-HDol).

	% Stabilization[c]				
Period of Irradiation[d]/h	2,4-HDol BCTMP[e]	AA BCTMP	2,4-HDol/AA BCTMP	1,4-PD BCTMP	A2,4-HDol BCTMP
1	76	62	74	45	65
2	71	59	74	36	64
4	65	48	72	36	56
8	61	--	--	--	--
16	41	--	--	--	--
22	--	29	--	--	--
24	--	--	--	--	29
Initial Brightness for Treated Handsheet[f]	85	88	85	88	88
Mass of Inhibitor applied (g/g handsheet)	0.028	0.032	0.058	0.021	0.042

[a]optical handsheets were prepared from a commercial BCTMP hardwood pulp following standard Tappi procedures; [b]handsheets were soaked in a methanolic solution for 1/4 h and then air and high-vacuum dried; [c]see equation 1 for a definition of % stabilization; [d]accelerated photo-aging was preformed with a Oriel Solar Simulator, and all experiments were preformed in triplicate; [e]BCTMP was prepared from hardwood; [f]Tappi and ISO Brightness measurements.

Table 5 Thermal Reversion Effects for BCTMP Handsheets[a] Treated with Methanolic[b] Solutions of trans,trans-2,4-hexadien-1-ol (2,4-HDol); trans,trans-2,4-hexadien-1-ol/Ascorbic Acid (AA); and Acetate of trans,trans-2,4-hexadien-1-ol (A2,4-HDol).

	Tappi Brightness			
Days in Darkroom[c]/h	2,4-HDol BCTMP[d]	Untreated BCTMP	2,4-HDol/AA BCTMP	A2,4-HDol BCTMP
0	88	87	87	84
3	85	87	--	--
6	--	--	86	--
7	--	--	--	84
8	84	86		
19	81	86		
87	76	85		
Mass of Inhibitor applied (g/g handsheet)	0.151	0.032		0.021

[a]optical handsheets were prepared from a commercial BCTMP hardwood pulp following standard Tappi procedures; [b]handsheets were soaked in a methanolic solution for 1/4 h and then air and high-vacuum dried; [c]all handsheets were stored in a darkroom, and all experiments were preformed in triplicate; [d]BCTMP was prepared from hardwood.

Photo-Reactivity of Chromophoric Structures

Introduction

Although the exact chemical reactions by which mechanical pulp undergoes photo-initiated deterioration remain ambiguous, certain important aspects of this process have now been determined[1]. The reaction is initiated by the absorption of a photon of light by extended conjugated structures present in lignin, such as α-carbonyl groups or olefinic structures conjugated with a phenyl ring. It has been proposed that the excited state of these compounds then leads to the formation of radicals either directly by an intramolecular bond cleavage process (path a, see below) or intermolecularly via abstraction of a phenolic hydrogen (path b). Alternatively, it has been suggested that the excited state could lead to the generation of singlet oxygen. This reactive species could react further with lignin (path c), generating a variety of radical intermediates. Recent research efforts by several investigators have challenged the proposed role of singlet oxygen in photoyellowing[2].

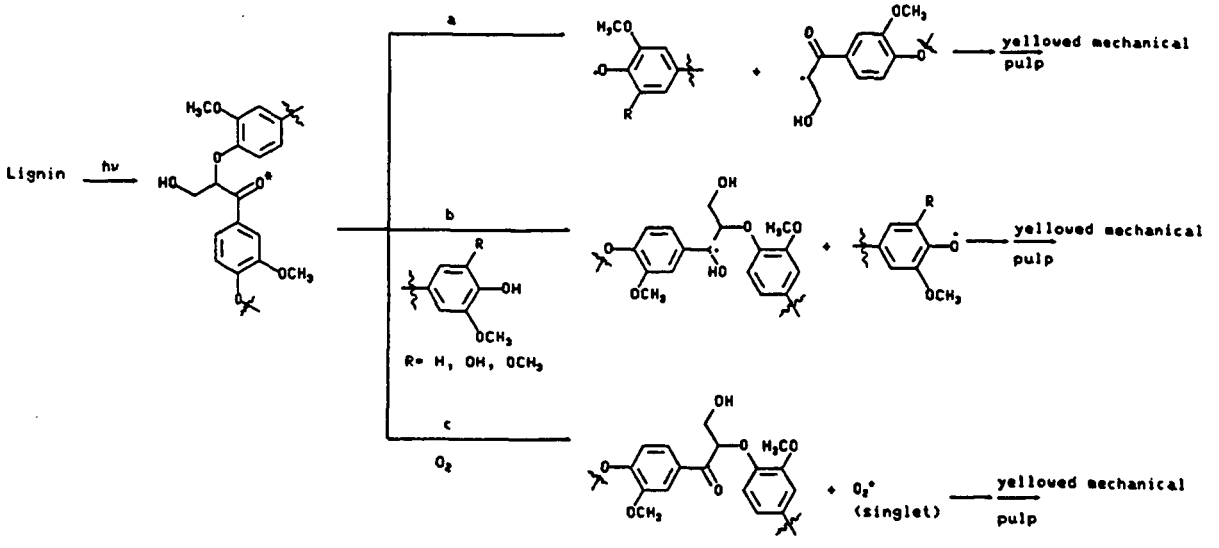


Figure 1: Proposed routes involved in the photo-aging of defiberlated wood.

Despite the results of model studies, the exact mechanism of photo-initiated oxidation of lignin in wood fibers remains uncertain. A recent paper by Francais et al[3] provided strong evidence for the intermediacy of hydroxyl radicals during brightness reversion of mechanical pulp. The authors therefore suggested that hydroxyl radicals (generated from

either pathway a or b in Figure 1) were major contributors to the photoyellowing of mechanical pulps. In direct contrast to these results, Fisher[4] has demonstrated that hydroxyl radicals and superoxide radicals can result in the bleaching of CTMP. The uncertainty about the reaction mechanisms contributing to the photo-aging of wood fibers was recently highlighted by Heitner[5] in his 1991 ISWPC plenary lecture in which he concluded that "very little is known about the key oxidation step of phenoxy free radicals to quinones."

Regardless of the reaction mechanisms responsible for generating the proposed radicals, it is generally accepted that these intermediates lead to the oxidative formation of *ortho*-[6] and *para*-quinones[7]. The presence of quinoid-like structures in photo-aged mechanical pulp has been supported by studies employing diffuse reflectance FT-IR, NMR, and UV spectroscopy techniques.

Several recent publications have suggested that quinones formed during brightness reversion contribute to subsequent photochemical reactions which further darken irradiated mechanical pulp[8]. If this suggestion were found to be generally true new mechanisms of photo-stabilizing mechanical could be designed. Research efforts from this laboratory have been directed at examining the photochemical behavior of *ortho*- and *para*-quinones believed to be present in photo-yellowed mechanical pulp handsheets.

Review of Past Project Activity

Previous research efforts in this area indicated that 2,6-dimethoxy-benzoquinone (DMBQ) was photo-stabile to the brightness reversion conditions. Samples of DMBQ applied to cotton linter handsheets and irradiated under the brightness reversion conditions did not undergo further photo-reversion. Furthermore, TMP handsheets treated with DMBQ and irradiated yellowed at a rates consistent with a reference handsheet. Both of these results suggested that DMBQ is not involved in subsequent photolysis reactions which could accelerate the rate of reversion. Applying the same experimental techniques with 2-methoxybenzoquinone (MMBQ) suggested that MMBQ is photo-reactive to the brightness reversion conditions.

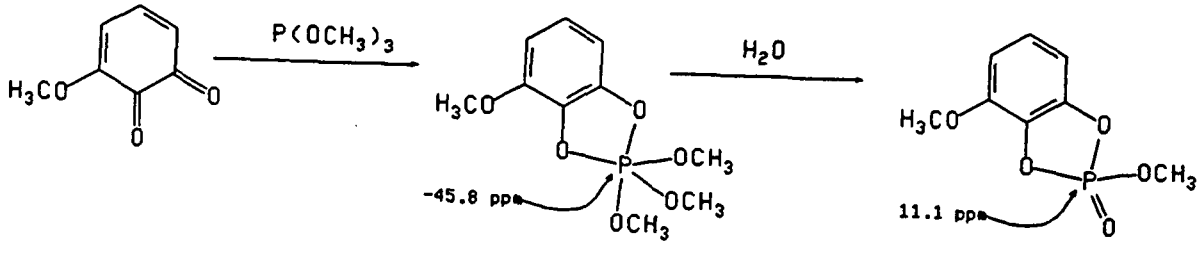
Discussions of 1991 Results

The photochemical behavior of 2,6-dimethoxy-3-hydroxybenzoquinone, 3-methoxy-*ortho*-quinone, and 4-methyl-*ortho*-quinone under the brightness reversion conditions was examined. The initial photochemical studies employed cotton linter handsheets doped with the quinones and irradiated with the Oriel Solar Simulator. As summarized in Table 1 all three compounds failed to darken the handsheets upon photolysis and indeed a mild brightening effect was noted. Similar results were noted when the compounds were applied onto BCTMP handsheets and are summarized in Table 2. The results of these

studies clearly suggest that not all quinones formed during brightness reversion are photo-reactive.

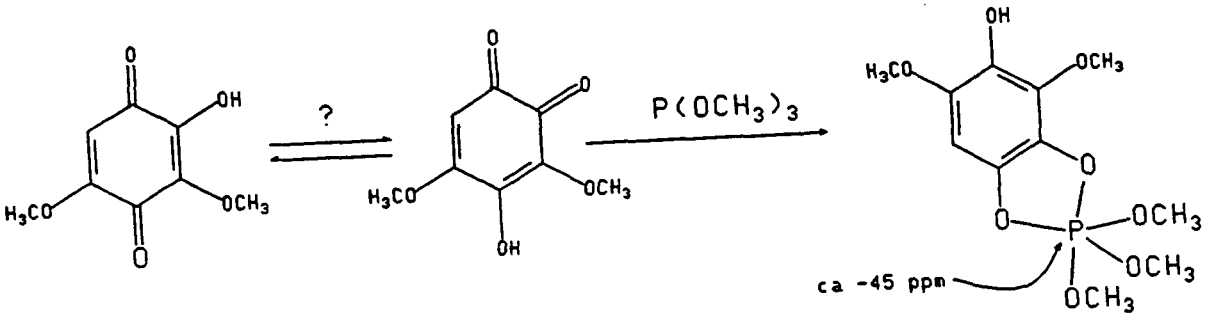
Further research efforts at determining the chemical mechanisms involved in darkening MMBQ doped cotton linter handsheets has inadvertently discovered a slow but significant thermal reversion process. Once this process was noted we pursued this observation by monitoring changes in brightness for MMBQ treated cotton linter and BCTMP handsheets. The results of these studies are summarized in Table 3. GC/MS analysis of the MMBQ spiked handsheets which have been "aged" for several days indicate the presence of dimeric MMBQ compounds. Analogous results have been noted by Forsskahl[9] during photo-reversion. This data is of importance in light of the fact that Forsskahl has proposed that the photo-reversion of MMBQ contributes to darkening of mechanical pulp handsheets. Although the rates of thermal reversion are not as significant as those reported for brightness reversion undoubtedly surface warming of MMBQ treated handsheets during the photolysis experiment would accelerate the thermal reversion phenomena. In conclusion the reported photo-yellowing of MMBQ spiked handsheets is most likely due to a complex series of thermal and photo-chemical reactions.

As discussed in the introduction to this section the detection of quinones in mechanical has been attempted with several spectroscopic techniques. Direct evidence for the presence of *ortho*-quinone structures in mechanical pulp was recently published by McDonough et al.[10] Their research efforts demonstrated that *ortho*-quinones found in mechanical pulp could be reductively O-alklylated and that the resulting products yielded diagnostic chemical shifts in the ^{31}P NMR, as summarized below.



The reactivity of trimethyl phosphite with *ortho*-quinones has now been employed by several researchers to characterize the types of chromophores generated during photo and thermal aging of mechanical pulp[11].

Our interest in this technique was focused on the potential reactivity of hydroxy *para*-quinones to also undergo an analogous type reaction with $P(OCH_3)_3$ to yield the reduced cyclic phosphate compound, as summarized below.



If this reaction were to occur then the diagnostic signals in the ^{31}P NMR at ca -45 ppm could be attributed to either *ortho*-quinones or 2-hydroxy-*para*-quinones. Given the increasing use of $P(OCH_3)_3$ as a test for the presence of *ortho*-quinones it was of interest to characterize this potential reaction.

The addition of $P(OCH_3)_3$ to either 2,6-dimethoxy-3-hydroxybenzoquinone in CD_2Cl_2 (solution is a deep red color) or 2,5-dihydroxybenzoquinone in CD_2Cl_2 (solution is yellow colored) yielded a clear, colorless solution within a few minutes. The change in color suggested that the quinones had been reduced by the trimethyl phosphite but it was unclear if these substrates had reacted according to the *ortho*-quinone pathway or *para*-quinone pathway. The ^{31}P NMR spectra of these reaction mixtures are shown in Figure 1. The NMR chemical shift data includes a strong signal at -45.2 ppm for 2,6-dimethoxy-3-hydroxybenzoquinone and -41.6 ppm for 2,5-dihydroxybenzoquinone. These results clearly demonstrate that hydroxy-para-benzoquinones can react in a manner similar to *ortho*-quinones. Hence the diagnostic signals in the ^{31}P NMR spectrum of mechanical pulp samples photo-aged and treated with $P(OCH_3)_3$ could arise from either *ortho*-quinones or hydroxy-*para*-benzoquinones.

Conclusions and Recommedations

The research efforts described in this section have demonstrated that not all quinone structures which may be present in mechanical pulp contribute to further photo-yellowung of mechanical pulp. Experimental data for MMBQ suggests that this component could contribute both to thermal and photo-reversion. The thermal-reversion component of MMBQ has not been previously reported and these results add to the complexity of of MMBQ and its role in brightness reversion.

The reaction of trimethoxy phosphite with hydroxy-*para*-benzoquinones has been shown to yield the reduced cyclic phospate which has a diagnostic signal at ca -45 ppm. These results are of significance in regards to characterizing quinone like structures found in mechanical pulp samples.

Future Activity

Research efforts in this area are currently focused on completing several minor issues associated with the photolytic behaviour of *ortho*- and *para*-quinones. Once these research studies are completed the results will be summarized in a publication and no further research efforts are currently anticipated in this field as all of the orginal goals have been completed.

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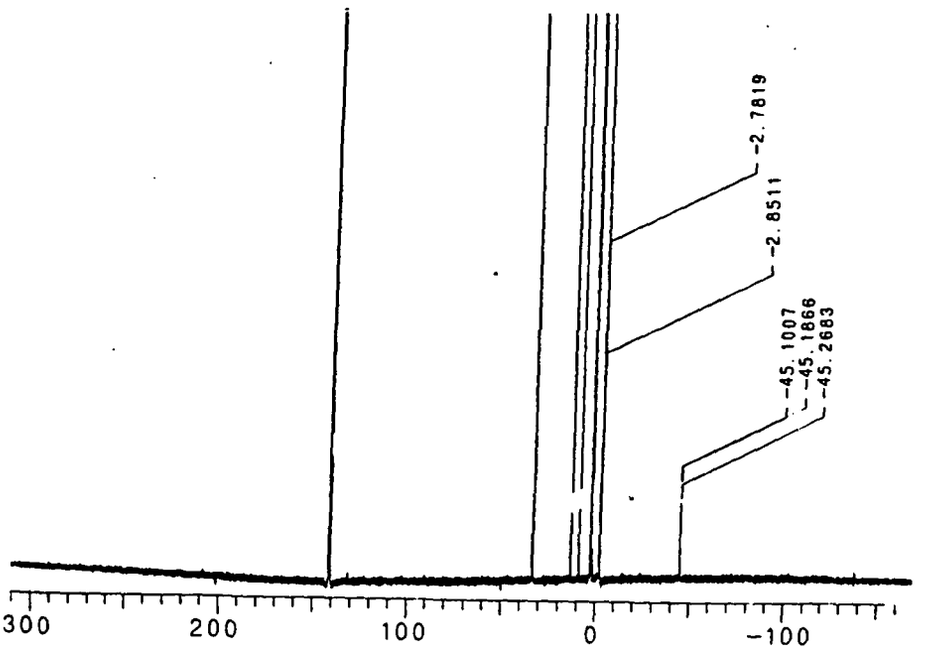
NMR Sample: $P(OCH_3)_3/CD_2Cl_2$/2,6-dimethoxy-3-hydroxybenzoquinone



NMR Sample: $P(OCH_3)_3/CD_2Cl_2$/2,5-dihydroxybenzoquinone

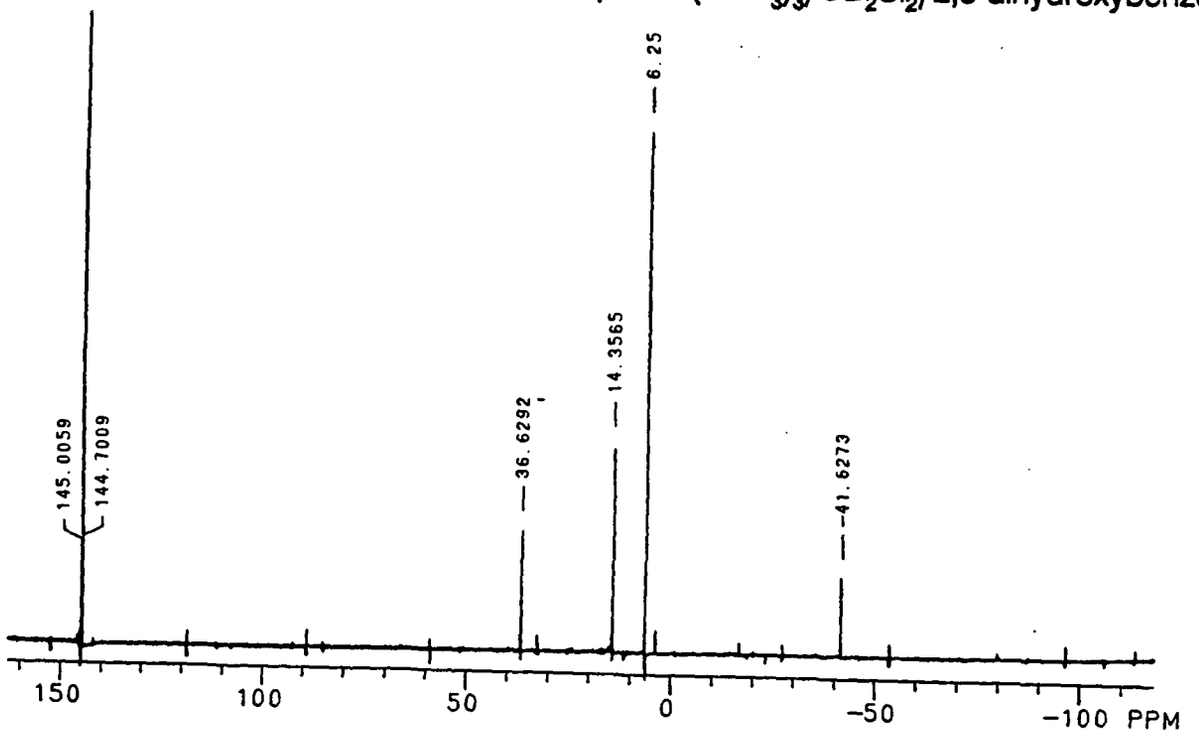


Figure 1 ^{31}P NMR Spectra

Table 1 Photolysis of Cotton Linter Handsheets(CLHS)[a] Treated[b] with 2,6-dimethoxy-3-hydroxybenzoquinone (DMBQ-3-OH); 3-methoxy-*ortho*-quinone (MMOQ); and 4-methyl-*ortho*-quinone (4-MOQ).

	ISO Brightness			
Period of Irradiation[c]/h	CLHS	DMBQ-3-OH/CLHS	MMOQ/CLHS	4-MOQ/CLHS
0	85	68	54	64
1	85	74	54	66
2	85	78	56	68
4	85	81	60	69

[a]optical handsheets were prepared from a commercial source of cotton linters, the linters were extracted with [1)]CH_2Cl_2, [2)]CH_3OH; [b]handsheets were soaked in a CH_2Cl_2 solution for 1/4 h and then air and high vacuum dried; [c]accelerated photo-aging was preformed with a Oriel Solar Simulator and all experiments were preformed in triplicate

Table 2 Photolysis of Cotton Linter Handsheets(CLHS)[a] Treated[b] with 3-methoxy-*ortho*-quinone (MMOQ); and 4-methyl-*ortho*-quinone (4-MOQ).

	ISO Brightness			
Period of Irradiation	Reference MMOQ	MMOQ/BCTMP	Reference 4-MOQ	4-MOQ/BCTMP
0	87	46	86	48
1	77	50	77	52
2	74	50	73	49
4	72	50	70	47

[a]optical handsheets were prepared from a commercial source of cotton linters, the linters were extracted with [1)]CH_2Cl_2, [2)]CH_3OH; [b]handsheets were soaked in a CH_2Cl_2 solution for 1/4 h and then air and high vacuum dried; [c] accelerated photo-aging was preformed with a Oriel Solar Simulator and all experiments were preformed in triplicate

Table 3 Thermal Reversion of 2-Methoxybenzoquinone (MMBQ) Applied[a] Onto Cotton Linter[b] and BCTMP Handsheets

Time in Dark Room[c]/h	MMBQ/Cotton Linter Handsheets	MMBQ/BCTMP[d] Handsheets
0	69	50
6	--	50
24	66	49
48	62	47
72	--	46
96	53	--
144	--	45
192	49	--
240	--	44
Initial Brightness Prior Application of MMBQ	86	86
Mass MMBQ/ g handsheet	0.021	0.018

[a]optical handsheets were prepared from a commercial source of cotton linters, the linters were extracted with [1)]CH_2Cl_2, [2)]CH_3OH; [b]handsheets were soaked in a CH_2Cl_2 solution for 1/4 h and then air and high vacuum dried;[c]all handsheets were stored in a darkroom, and all experiments were preformed in triplicate; [d]BCTMP was prepared from hardwood.

Photo-Formation of Chromophoric Structures

Introduction

Current theories of brightness reversion have been developed from extensive model compound work. The photo-reactivity of α-carbonyl groups has been extensively studied by several research groups. Grier and Lin[1] demonstrated that several phenacyl-α-O-arylethers compounds were photo-labile and rapidly yellowed when irradiated with near-UV light. Castellan[2] further explored the photo-reactivity of these compounds both in solution and absorbed onto cellulose fibers. Characterization of the products formed from photolysis are consistent with an initial homolytic rupture of the β-O-aryl ether bond and subsequent radical coupling and rearrangement reactions. In addition to these low-molecular-weight products, a larger oligomer component is always found in yields varying from 10% - 50%. Castellan[3] has characterized this component and shown that peak molecular weight for the oligomer varies from 2667 to 4275 depending on the reaction medium employed (i.e. chemical fibers --> benzene). Analysis of the photolysis product mixture indicates that the oligomer portion is the principal component contributing to the yellowing of the product mixture[4]. Furthermore, it has been postulated that the oligomers are formed from the reactive species generated during photolysis, such as radicals, phenols, and quinones[3].

The photoreactivity of other chromophoric compounds[5], such as biphenyl and stilbene derived lignin type structures, has also been shown to undergo rapid light-induced yellowing when exposed to UV light at wavelengths > 300 nm. These results clearly suggest that several structural subunits commonly found in lignin are prone to photo-chemical reactions under the conditions found to initiate photo-aging of wood.
Regardless of the reaction mechanisms responsible for generating the proposed radicals, it is generally accepted that these intermediates lead to the oxidative formation of *ortho*-[6] and *para*-quinones[7].

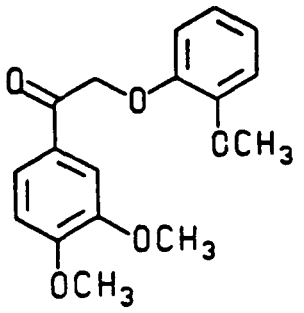
Our principal research interest in this area was to determine if the photolysis (λ = 300 - 400 nm) of these types of compounds did indeed yield *ortho*-quinone like structures in the colored oligomeric product. Since these types of structures have been detected in photo-aged mechanical pulp, it was of concern to determine if current model studies also yield *ortho*-quinones. To date, the presence of these structures has not been detected in the photolysis of model compounds, although it has been proposed that these types of structures are incorporated into the colored oligomeric component generated during photolysis.

Review of Past Project Activity

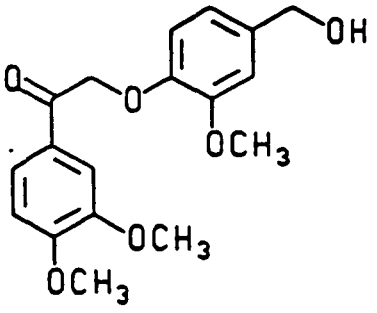
Previous research efforts in this area have been focused principally on preparing a series of lignin dimeric and trimeric compounds. The photolytic behavior of these compounds has been explored and shown to be consistent with previously reported literature results.

Discussions of 1991 Results

Research efforts over the last year have been directed at determining if the photolysis of lignin model compounds I and II (see below) do indeed yield a oligomeric product which contains quinone-like structures.



I



II

The experimental approach that was employed consisted of photolyzing samples of A or B absorbed onto cotton linters. The products from photolysis were extracted with dichloromethane, concentrated, and treated with trimethyl phosphite. The total reaction mixture was then examined by ^{31}P NMR. Employing this approach the presence of *ortho*-quinones should be readily detected (for an expanded discussion on the use of ^{31}P NMR and trimethyl phosphite to detect *ortho*-quinones refer to the previous section).

It was therefore much to our surprise that when either I or II absorbed on cellulose was photolyzed, extracted, and treated with $P(OCH_3)_3$ the resulting ^{31}P NMR spectrum, shown below, does not contain a signal at -45 ppm (see Figure 1). Although initially we attributed this to hydrolysis of the cyclic phosphorous compound, the addition of 3,5-di-t-butyl-1,2-benzoquinone yielded the diagnostic signal at -47.0 ppm. These results clearly suggest that if the photolysis experiment had yielded an *ortho*-quinone it would have been detected in the $P(OCH_3)_3/^{31}P$ NMR experiment. To explore the potential that the *ortho*-quinones generated were unstable to subsequent photo-chemical and/or thermal reactions, we have photolyzed mixtures of I and 3-methoxy-1,2-benzoquinone. Following the same experimental procedure as above, the ^{31}P NMR spectrum contained a signal at -44.2 ppm, as shown below (see Figure 1, NB: signals at 2.6 and 10.9 were shown not to be due to the lignin model compound or its photolysis products).

Initially, the deficiency of a signal in the NMR spectra for *ortho*-quinone-like structure was thought to be due to the fact the photolysis of I or II was preformed in the absence of lignin like structures. Therefore the photolysis reactions were repeated in the presence of 4-hydroxy-3-methoxybenzyl alcohol, 3-hydroxy-4-methoxybenzyl alcohol and 4-hydroxy-3-methoxy-methylbenzene. Analysis of these reaction mixtures employing the above procedures also failed to detect any signals which could be attributed to the *ortho*-quinone structure.

Conclusions and Recommendations

These results clearly demonstrate that the current model compounds employed to study brightness reversion fail to yield one of the most important chromophoric structures involved in brightness reversion. The results of these studies support Heitner's[32] contention that the exact chemical mechanisms involved in oxidizing phenolic structures to quinones are far from understood. Due to the important role that quinones have in the brightness reversion phenomenon it is urgently needed that further studies be preformed so as to develop an understanding of their mechanisms of formation.

Future Activity

Future research efforts will examine the products formed from the photolysis of lignin trimers. Studies directed at understanding how the ultrastructure of wood fibers may influence the photo-reactivity of α-carbonyl groups will also be examined.

Collectively, these investigations will provide fundamental investigations as to what is occurring in the chemically complex nature of mechanical pulp when it is irradiated. These studies will support our current efforts at designing novel methods of retarding the brightness reversion process.

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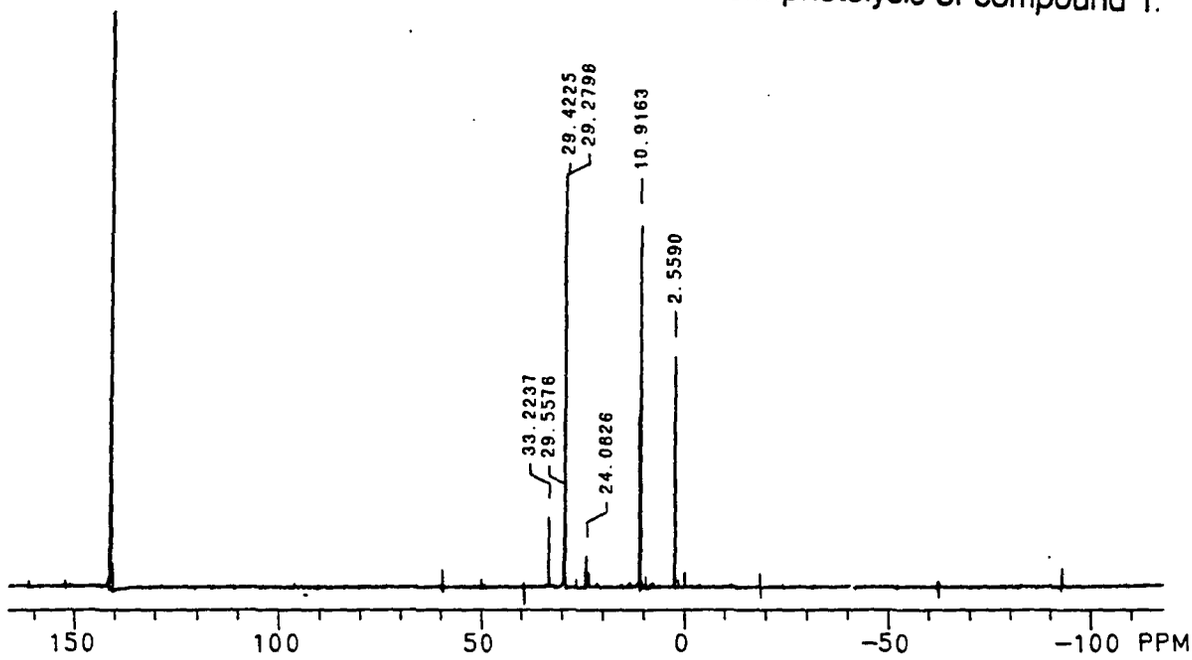
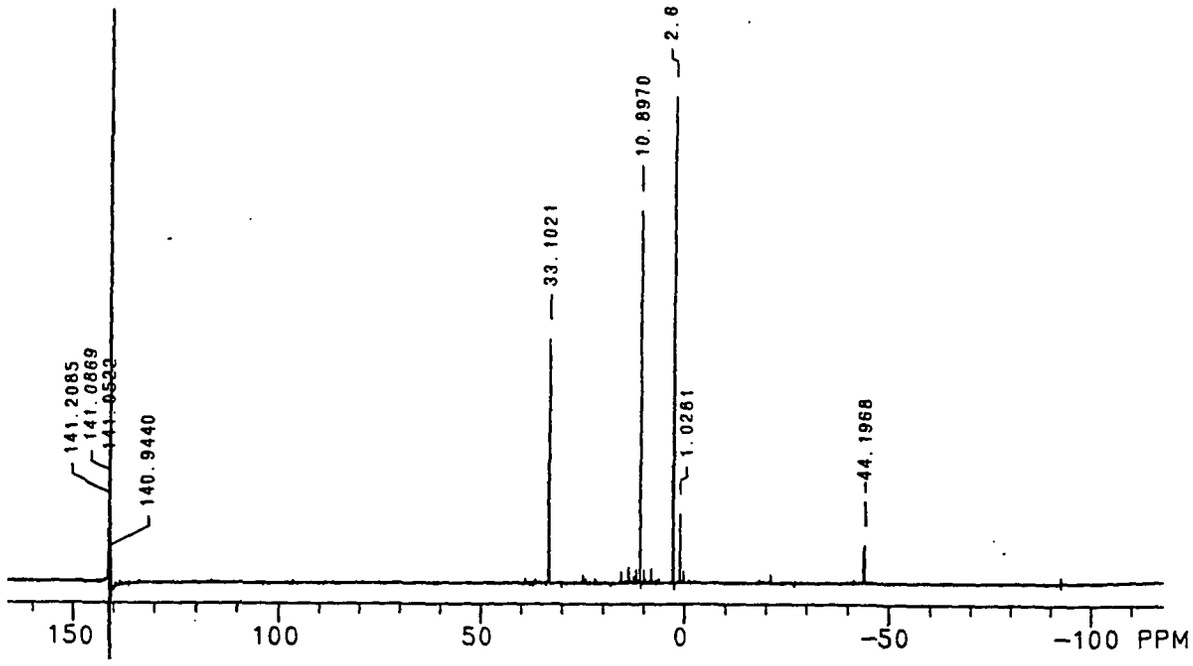
^{31}P NMR of the $P(OME)_3$ derivatives formed from photolysis of compound 1.





^{31}P NMR of the $P(OME)_3$ derivatives formed from the photolysis of compound 1 and 3-methoxy-1,2-benzoquinone.

Figure 1 ^{31}P NMR Spectra

PROJECT 3694

HIGH BRIGHTNESS HIGH YIELD PULPS

RESEARCH REVIEW

MARCH 24, 1992

Alan W. Rudie and Thomas J. McDonough

Technical Program Review Report

PROJECT TITLE: High Brightness High Yield Pulps

PROJECT STAFF: A. W. Rudie and T. J. McDonough

BUDGET (FY 91-92): $100,000

REPORTING PERIOD: March 1991 - March 1992

DIVISION: Chemical and Biological Sciences Division

PROJECT CODE: HBRIT

PROJECT NUMBER: 3694

OBJECTIVE: Develop a cost effective method to produce high yield pulps of high and stable brightness.

GOAL: A significant increase in brightness and a decrease in bleaching cost for high yield pulps.

SUMMARY:

Initial project work (FYS 89-91) focussed on the utility of molecular oxygen as a bleaching treatment for high yield pulps. It was found that molecular oxygen gave a 1 to 2 point increase in pulp brightness at near neutral pH (5 - 8) but that the increase was not additive with other bleaching methods. Treatment of pulp with oxygen and hydrogen peroxide simultaneously showed that oxygen does contribute a point in brightness in peroxide bleaching, but that sufficient oxygen was supplied by peroxide decomposition and atmospheric sources and the contribution was only apparent relative to a control conducted under nitrogen.

The project focus this year has been on bleaching with alternative peroxides to determine if greater efficiency can be obtained, or lower cost sources of peroxide identified. Experiments carried out with 1% hydrogen peroxide and 0.1% molybdenum trioxide as an activation catalyst all gave a 10 to 15 point loss in brightness. Since the molybdenum content remaining on pulp was low, this result is evidence of an altered peroxide reactivity that is undesirable.

Experiments carried out with peracetic acid were more successful. Bleaching with 1% peracetic acid (0.013 moles per 100g OD pulp) at a starting pH of 8.5 and using sodium dihydrogen phosphate as stabilizer gave a brightness gain of 6.3 points GE. This compares to a brightness gain of 7.2 points GE when using 0.5% hydrogen peroxide (0.015 moles per 100 g OD pulp). From this it was concluded that peracetic acid was about half as effective as hydrogen peroxide at bleaching high yield pulps on a weight basis, and approximately equivalent to hydrogen peroxide on an equimolar basis. Follow up experiments with hydrogen peroxide showed no synergism between the peracetic acid and hydrogen peroxide. Peracetic acid is ineffective at increasing brightness as a second stage bleaching chemical following hydrogen peroxide, and at high peroxide charges, actually reduces brightness. As a first stage treatment, preceding hydrogen peroxide, peracetic acid does bleach TMP, but cannot increase brightness beyond that obtained with a single stage hydrogen peroxide treatment.

The conclusion from this effort is that alternative peroxide chemistry is not likely to give an increase in molar bleaching efficiency, and the project should focus on reducing peroxide costs.

A review of the autoxidation literature and chemical cost data identified butadiene as an inexpensive chemical that is readily oxidized by air to give peroxides in 50% yield. Since the oxidation conditions for butadiene are above it's flash point and within it's explosive limits, we have attempted to investigate this chemistry using other chemicals that can be handled safely in the laboratory. Attempts to oxidize 2,4-hexadienoic acid (sorbic acid) suspended in water gave very low yields of peroxides. Attempts to bleach pulp by *in-situ* oxidation of sorbic acid gave similar brightness response to the control experiments without added sorbic acid.

Attempts to generate peroxides by autoxidation of 1,2,4,5-tetramethyl-1,4-cyclohexadiene met with similar results. A more detailed attempt was made to understand the course of the autoxidation reaction of 1,5-cyclooctadiene (COD). The unstabilized COD reacts within two hours to give 5-10% conversion to peroxides. Prolonged reaction periods give no further increase in peroxide activity. Thin layer chromatography (TLC) has shown that there are at least 3 products of the autoxidation reaction, only one of which reacts with potassium iodide. Efforts to concentrate the peroxide product by chromatography have been unsuccessful.

Future efforts are to focus on finishing an evaluation of organic peroxide bleaching efficiency using commercial organic peroxides (t-butyl hydroperoxide and t-butyl peroxide) and a readily isolated peroxide of methyl linoleate. If these peroxides show bleaching activity approaching that of hydrogen peroxide on an equimolar basis, the project will need to locate a cooperator with pressure vessels suitable for preparing the butadiene peroxide.

INTRODUCTION

For years, the rallying cry of high yield pulping research has been 90-90-9; 90 points brightness, 90% yield and 9 km breaking length. Although still far from 90 GE brightness and 9 km breaking length, market aspen CTMP at 80 - 85 ISO brightness and 6 km breaking length[1] is approaching the most significant properties of the bleached kraft hardwood pulps used in many integrated southern mills[2]. We are seeing a shift in R & D emphasis to other characteristics of high yield pulps that still fall far short of chemical pulp performance. At present, the brightness reversion of high yield pulps is considered to be the primary characteristic preventing bleached aspen CTMP from making significant inroads into the printing and writing papers market[3].

Although brightness reversion is a significant barrier to market penetration in some paper grades, in the U.S., the problem is a bit more basic, high brightness CTMP simply costs too much. With a specific energy requirement of 1000 kWh/BDT and bleach requirement of 3-4% hydrogen peroxide, the manufacturing costs of CTMP approaches or exceeds the manufacturing cost of hardwood kraft pulp in much the country.

The obvious means to reduce the manufacturing costs of high yield pulps in the U.S. are to reduce the electrical energy requirements of the process or reduce the expense of bleaching to high brightness. This project is concerned with investigating alternative bleaching processes with potential to reduce bleaching costs and/or increase bleached brightness in high yield pulps.

REVIEW OF PAST PROJECT ACTIVITY

Several series of experiments have been performed to evaluate oxygen and peroxide bleaching through a range of starting pH. Initial results were interesting but the project was unable to identify oxygen/peroxide treatment conditions that give an overall brightness gain relative to conventional peroxide bleaching.

News grade TMP treated with 80 psig oxygen at 80° C for 90 minutes showed increases in brightness when the starting pH was adjusted to between 5 and 8. Experiments using both oxygen and peroxide at pH 8 gave the best brightness gain, 8 points. relative to the unbleached control. Samples that were bleached with 1% hydrogen peroxide after the oxygen treatment all gave an additional 10 to 11 point brightness gain with the total brightness gain relative to the unbleached pulp of about 12 points. After some effort to optimize the treatment conditions, it was determined that the addition of oxygen under pressure was of minimal benefit and that the bleaching results and peroxide residuals were within experimental error of the control experiments. Experiments conducted using 120 psig oxygen at 120° C lost brightness at all starting pH levels investigated.

Although the high pressure oxygen experiments did not demonstrate a commercially attractive result, experiments at atmospheric pressure showed a one point decrease in brightness gain when peroxide bleaching was conducted under nitrogen (Table 1). This observation may be of interest to existing mills currently adding steam to the peroxide mixer. The addition of steam at the entry to the peroxide bleach tower may reduce the atmospheric oxygen content below desirable levels and result in a slight decrease in bleach plant performance.

Table 1. Influence of Atmosphere on Peroxide Bleaching

	Bleaching Atmosphere		
% NaOH	Nitrogen	Bag Bleach	Oxygen
2.5%	70.5	-	74.3
3.5	73.8	74.4	74.5
4.0	72.4	72.6	73.2
4.5	69.4	-	69.8

All bleaches carried out using a pilot plant southern pine TMP of starting brightness 55.7 GE. Pulp was pre-treated with DTPA and bleached with 4% hydrogen peroxide, 3% sodium silicate and 0.05% magnesium sulfate on OD pulp. Several entries are the average of two or more experiments. The bag bleach brightness are estimated by interpolating between a brightness obtained after 90 minutes and after 180 minutes.

DISCUSSION OF 1991 RESULTS

Since the review of oxygen as a bleaching or bleach assist chemical was largely unsuccessful, it was decided to investigate the potential to activate oxygen by reaction with readily oxidized (autoxidized) organic materials to form organic peroxides. The initial experiments were undertaken to determine the molar bleaching efficiency to be expected from organic peroxides. Although some information is available in the literature[4,5], it was difficult to compare efficiencies directly with hydrogen peroxide and it was decided to repeat some of this work.

Peroxide Activation With Molybdenum Trioxide

An initial attempt to modify the reaction chemistry of hydrogen peroxide was carried out by adding molybdenum trioxide as an activation catalyst. All samples lost brightness, finishing up with a distinct red color (Hunter a = 6.2 to 9.0). This was initially assumed to be due to molybdenum remaining with the pulp but since the residual Mo analysis is around 5 ppm, the

loss in brightness and red color are considered indicative of a detrimental change in the peroxide chemistry. These results are reported in table 2. A recent article suggests that this pulp may bleach favorably in a second stage hydrogen peroxide treatment[6] and this may be worthy of further review.

Table 2. Peroxide bleaching with MoO_3 catalyst.

pH	final pH	Residual Peroxide	TAPPI Brightness	Hunter	Hunter a	Hunter b
Starting Brightness			49.0			
3.0	3.0	0.63	37.8	75.1	7.1	17.8
5.0	3.1	0.59	38.5	75.3	7.0	17.5
7.0	3.2	0.39	35.5	72.9	7.2	17.4

All samples pretreated with 0.1% DTPA at pH 2.0, 3% consistency, 50° C for 2 hours. Samples were filtered and dewatered to 25% consistency. Bleaching conducted at 20% consistency using 1% hydrogen peroxide, 0.1% MoO_3, 0.1% DTPA, 60° C for three hours.

Bleaching TMP With Peroxyacetic Acid

Peroxyacetic acid has been known to bleach high yield pulps since at least 1944.[7] Typical oxidation chemistry of peroxyacetic acid is quite different from hydrogen peroxide. Peroxyacetic acid is commonly used in the Baeyer-Villiger oxidation of ketones to lactones and epoxidation of olefins, neither of which can be carried out using hydrogen peroxide without a catalyst[8]. Peracid also readily delignifies wood under mildly acidic conditions.[9]

A series of bleaching experiments was conducted to evaluate the bleaching potential of peracetic acid relative to hydrogen peroxide. The initial series investigated several stabilization options. For these experiments a target starting pH of 8.5 was selected based on the optimum bleaching response reported in the literature.[10] Pulp was pretreated with a reduced charge of DTPA (0.05% on OD pulp) and bleached with 1% peracetic acid (0.13 moles per 100 g of OD pulp). Sodium dihydrogen phosphate, sodium tripolyphosphate, and sodium silicate were evaluated as buffers and stabilizers. These results are reported in table 3.

The highest brightness (57.6 TAPPI brightness, 6.3 points brightness gain) was obtained using sodium dihydrogen phosphate. A conventional hydrogen peroxide control experiment using 0.5% hydrogen peroxide (0.14 mole per 100 g of OD pulp gave) a final brightness nearly a full point higher at 58.5.

Table 3. Single stage bleaching with peracetic acid

Additive	TAPPI Brightness	pH off	Peroxide Residual	Hunter L	Hunter a	Hunter b
Control	51.3			84.1	0.58	16.8
None	55.0	5.5	0.02%	85.7	0.0	16.0
NaH_2PO_4	57.6	5.8	0.04	86.8	0.0	15.3
$Na_5P_3O_{10}$	55.9	5.5	trace	86.4	0.13	16.0
Silicate	56.6	7.0	trace	86.4	0.0	15.5
H_2O_2	58.5	9.6	0.05	87.2	-0.8	15.2

Pulp was pretreated with 0.05% DTPA at pH 2.0 and 40° C for 60 minutes. Bleaching was carried out using 1% peracetic acid at a starting pH of 8.5 and 20% pulp consistency. The bleach temperature was 40° C with a retention time of 90 minutes. Sodium dihydrogen phosphate was added at a rate of 0.5% on pulp, sodium tripolyphosphate at 0.2% on pulp, and sodium silicate at 3.0% on pulp. The peroxide control experiment was bleached with 0.5% hydrogen peroxide using 3% silicate and 0.05% magnesium sulfate as stabilizers.

In a second series of experiments, 1% peracetic acid was evaluated as a second stage bleach treatment following a conventional hydrogen peroxide stage using 1% H_2O_2 on pulp. The best result gave a 10 point brightness gain, exceeding the brightness obtained in a 1% hydrogen peroxide control experiment by 1 point. The peroxide control conducted with 1.45% peroxide on pulp (equimolar to the peracid experiments) gave a final brightness of 64.5, one point higher than obtained with the two stage process. This data is reported in table 4.

Table 4. Peracetic acid as a second stage following hydrogen peroxide.

% NaOH	TAPPI Brightness	pH off	Peroxide Residual	Hunter L	Hunter a	Hunter b
Start	53.4			85.4	0.89	16.5
1.0	62.9	6.5	0.3	89.4	-1.0	14.2
0.75	62.1	6.3	0.5	88.9	-0.7	14.5
1.2	63.4	6.6	0.2	89.6	-1.0	14.2
1% H_2O_2	62.8	8.2	0.2	89.5	-0.8	14.5
1.4% H_2O_2	64.5	8.0	0.4	90.0	-1.2	14.2

All samples pretreated with 0.25% DTPA. First stage is 1% H_2O_2, 3% silicate, 0.05% $MgSO_4$, 20% consistency, 60° C for 90 minutes. Second stage is 1% peracetic acid 10 % consistency, 40° C for 90 minutes. The pulp was not washed between stages but pH was adjusted to 8.5 before adding the peroxyacetic acid. For the two control experiments, the caustic charge was the same as the peroxide charge.

Several more experiments were conducted to determine if peracid was effective as a second stage following higher charges of peroxide. All samples lost brightness in the peracetic acid treatment. The principle difference in technique between the first and second series of experiments is that the initial hydrogen peroxide stage was ninety minutes in the first series and 3 hours in the second. Since the pulp is not washed between stages, the samples treated for just 90 minutes would gain another one to two points in brightness if the retention time were extended to 3 hours. The peracetic acid does not have to contribute to the bleaching process to obtain a brightness increase. In the second series of experiments, the initial 3 hour peroxide stage exhausts the bleaching potential of the peroxide and it cannot contribute much to brightness gain during the peracid stage. These results are reported in table 5.

Table 5. Peracetic acid following peroxide as a second stage.

stage	% H_2O_2	% NaOH	pH off	TAPPI Brightness	% Peroxide Residual
1	2.0	1.4	8.1	67.2	0.52
2			4.7	66.2	1.0
1	3.0	2.6	8.4	70.5	0.6
2			4.8	69.7	1.0
1	4.0	3.0	8.8	72.4	0.9
2			5.5	70.6	1.4
Control	5.0	4.4	9.8	73.2	0.8

All conditions are the same as in table 4 except that the first stage peroxide treatment was for 3 hours.

In a final series of experiments, 1% peracetic acid was evaluated as the initial stage followed by 1% hydrogen peroxide as the second stage in a two stage bleaching sequence. Since the optimum pH for the initial peracid stage in the two stage sequence may not give maximum brightness from this stage, the initial pH was varied over a wide range. After the peracid stage, the pulp was treated with a conventional peroxide bleach solution. The second stage caustic charge was adjusted for a target final pH between 8.0 and 9.5. The maximum brightness gained was 9.8 points in TAPPI brightness compared to 9.9 points gain in a conventional single stage experiment using 1.45% (equimolar) hydrogen peroxide. Adding the maximum brightness gained in the first stage (3.8 points) with the maximum gained in the second stage (7.1 points) would only give a one point advantage over the single stage peroxide control. This is considered an insufficient advantage to continue pursuing the two stage process. Results of this series of experiments are reported in table 6.

Table 6. Peracetic acid preceding peroxide in two stage bleaching

Stage	NaOH	pH on	pH off	TAPPI Brightness	Residual Peroxide
1	-	-	2.6	53.8	0.21
2	1.9		5.9	59.5	0.78
1	-	6.0	4.3	57.1	0.15
2	2.7		8.1	64.2	0.16
1	-	9.9	5.2	58.2	0.0
2	2.0		8.3	63.3	0.08
Control	1.4		7.9	64.3	0.47
Starting				54.4	

All samples were pretreated with 0.25% DTPA at pH 2.0 for 1 hour. The peracetic acid stage was conducted using 1% peracetic acid and 0.5% sodium dihydrogenphosphate at 20% consistency, 40° C for 120 minutes. The second stage was carried out with 1% hydrogen peroxide, 3% sodium silicate, 0.05% magnesium sulfate, 180 minutes at 60° C. Bleach consistency was approximately 18%. The control was conducted with 1.45% hydrogen peroxide with all other conditions the same as the second stage.

The conclusion reached thus far is that peracetic acid has at best, the same molar efficiency for bleaching TMP as hydrogen peroxide. Assuming that other organic peroxides would react following general mechanisms similar to either hydrogen peroxide or peracetic acid, the choice of autoxidizable organic compounds for lower cost bleaching will be dictated by cost and yield.

Autoxidation of Organic Compounds

A review of organic chemical prices in the Chemical Marketing Reporter, and of the autoxidation literature indicated that butadiene has a high probability of forming cost effective peroxides. Butadiene is commercially available for about $0.16 a pound. It readily oxidizes to a viscous butadiene peroxide polymer and yields above 50% have been reported.[11] At 50% conversion, a butadiene peroxide will cost about 4 cents per gram mole compared to about 5 cents per gram mole for hydrogen peroxide. Since the butadiene is readily separated from the peroxide, higher overall conversion rates and improved economy are likely. Unfortunately, the butadiene peroxide is explosive if improperly handled[12] and any commercial applications will have to be carefully designed.

Given the explosive nature of butadiene peroxide, and the need to operate the oxidation process above the flash point and within the explosive limits of butadiene, it was decided to evaluate other organic peroxides that could be handled more safely, before attempting to work with butadiene.

Autoxidation of 2,4-hexadienoic Acid

2,4-hexadienoic acid (sorbic acid) is a six carbon conjugated diene that because of the carboxylic acid functional group, has low volatility, a high flash point and is slightly soluble in water. In the initial experiments, sorbic acid was suspended in 100 ml of water (or 0.1 N NaOH) and the solution stirred under oxygen for 24 hours. In all cases a few TMP fibers were added to provide a free radical initiator. Results of these experiments are summarized in table 8. Yields of peroxide are low and were considered insufficient to proceed with bleaching experiments using the products. Instead it was decided to evaluate the use of sorbic acid autoxidation *in-situ* with pulp to determine if it would participate in pulp bleaching reactions with oxygen.

Table 8. Autoxidation of Sorbic Acid

Exp.	Solvent	O_2 (psig)	° C	% R_1OOR_2
1	0.1N NaOH	35	65	1%
2	H_2O_2	80	80	8%
3	0.1N NaOH	80	80	15%

Conditions: All reactions were conducted using 1.12 g (10 mmole) of sorbic acid dispersed in 100 ml of solvent. Yield of peroxide is based on concentration in recovered solvent, not total recovery. Yields are maximum possible yield, in all cases there is some loss of solvent.

In these experiments, 5% sorbic acid was mixed with pulp along with 2% hydrogen peroxide, 3% silicate and 0.05% Magnesium sulfate. The alkali charge was varied from 3.5 to 6.5%. Each sample was mixed in a Hobart® mixer at 20% consistency, loaded in a wire mesh tray and place in the pilot plant high consistency oxygen reactor. Also loaded into the reactor were three identical trays of pulp without the sorbic acid to serve as control experiments. In addition, three conventional peroxide bleaches were carried out in plastic bags to determine the standard bleach response of the pulp to 2% hydrogen peroxide. The results (table 9) suggest that the sorbic acid has not contributed to additional bleaching under these conditions. A second series of experiments carried out at 100° C gave similar results which are reported in table 10.

Two experiments were carried out to evaluate autoxidation of 1,2,4,5-tetramethyl-1,4-cyclohexadiene. Suspended in distilled water and oxidized at 65° C and 35 psi for 24 hours 1,2,4,5-tetramethyl-1,4-cyclohexadiene gave less than 1% conversion to peroxides. In 0.1N NaOH, the titrated yield of peroxide product was about 1%.

Table 9. *In situ* Autoxidation of sorbic acid

Sorbic Acid	% NaOH	TAPPI Brightness	pH off	% H_2O_2 Residual	Hunter		
					L	a	b
5 %	3.5	67.0	6.3	0.29	91.0	-0.9	13.1
5	4.5	66.7	8.8	0.1	91.3	-2.1	14.0
5	5.5	65.3	9.5	0.02	90.6	-1.2	14.1
5	6.5	58.6	9.7	0.003	87.6	-1.0	15.6
0	1.0	67.1	6.6	0.88	91.4	-1.0	13.6
0	1.5	68.3	7.1	0.6	91.9	-1.7	13.8
0	2.0	67.2	8.2	0.36	91.7	-2.0	14.0
C	1.5	66.5	8.1	0.81	91.0	-1.6	13.7
C	2.0	68.5	8.3	0.61	91.5	-1.5	12.8
C	2.5	68.7	8.7	0.44	91.9	-1.6	13.0

All experiments were carried out at 20% consistency, 80° C, 75 psig of oxygen for 90 minutes. All samples are pretreated with DTPA and contain 2% hydrogen peroxide, 3% silicate and 0.05% magnesium sulfate. Experiments labeled C are conventional peroxide bleach controls carried out in plastic bags at 20 % consistency, 65° C for 90 minutes. Starting pulp is a southern pine TMP of 54.6 TAPPI Brightness.

Table 10. *In situ* autoxidation with sorbic acid at 100° C

	% NaOH	TAPPI Brightness	pH off	Residual H_2O_2	Hunter		
					L	a	b
5	2.5	62.3	5.5	0.42	89.8	-1.3	15.5
5	3.5	62.6	6.1	0.22	90.3	-1.2	15.6
5	4.5	58.9	7.6	0.01	88.3	-1.0	16.2
5	4.0	62.2	6.9	0.07	90.1	-1.2	16.0
	1.0	64.2	6.0	0.56	90.6	-1.2	15.1
	1.5	64.6	6.4	0.4	91.2	-1.7	15.3
	2.0	63.2	6.8	0.18	90.7	-1.7	15.8
C	2.5	68.1	8.7	0.43	91.3	-1.5	12.9

All conditions are the same as in table 9 except the experiments were carried out at 100° C.

Several experiments have also been carried out on the autoxidation of 1,5-cyclooctadiene (COD). Since COD is insoluble in water, it was decided to perform the oxidations without a solvent. Several small beakers were each loaded with a few ml of COD and placed in the pressure vessel. Oxygen was added to a pressure of 30 psig. Samples were collected and titrated at 3 hours, 24 hours and 28 hours. The peroxide activity rose to 4% within three hours and remained approximately constant for the next 24 hours. Titration of the starting COD solution showed that it already contained 2% peroxide so very little additional conversion occurred in the pressure vessel.

Analysis of the oxidation products of COD by thin layer chromatography shows three materials. The first spot to separate on the tlc plate is readily eluted with hexane and is not active to KI/acetic acid. This is the bulk of the material and is assumed to be unreacted COD. The next spot is quite small, elutes slowly with hexane and more rapidly with the more polar solvents. It does not react with KI. The third spot cannot be eluted with hexane but is readily eluted with toluene, ethanol, methanol, diethyl ether or ethyl acetate. This compound react with KI to give a yellow spot and is assumed to be a peroxide.

A short column of silica gel was prepared from a hexane slurry and a sample of the oxidized COD added. This was eluted with two 200 ml samples of hexane. These fractions were analyzed by tlc and show only the starting COD and the second, unknown material. The column was then eluted with four 200 ml fractions of ethanol and each of these fractions checked by tlc. All four show some evidence of cyclooctadiene and the unknown compound. The first three fractions also contain the third compound identified by KI/acetic acid as a peroxide. Unfortunately, titration of these samples for peroxide gave unusual results. All four turned red after addition of the first few drops of thiosulfate. Addition of starch turned the solutions a red brown color. At the end of the titration, all four samples were still a light yellow instead of colorless and the fourth fraction required the largest amount of thiosulfate to reach the endpoint. Since this fraction does not give the third spot on tlc and neither of the two spots it does give react with KI, it is not thought to contain a peroxide and the meaning of the titration is unknown. Cyclooctadiene can form cyclic peroxides capable of decomposing to conjugated diketone products. These would be similar to quinone and can potentially form semiquinone type charge transfer complexes in intermediate oxidation states.

Experimental Procedures

General Procedures

Peracetic acid was obtained from Aldrich Chemical company as a 32% solution in dilute acetic acid. It was used without further purification and was titrated before use. Diethlylenetri-aminepentaacetic acid was also purchased from Aldrich. Sorbic acid was purchased from Sigma Chemical Company as 99+% purity. 1,2,4,5-tetramethyl-1,3-cyclohexadiene was kindly provided by Dr Art Ragauskas. 1,5-cyclooctadiene was purchased from Aldrich Chemical Co. as an unstabilized liquid packed under nitrogen. Molybdenum trioxide, sodium tripolyphosphate,

and sodium phosphate monobasic were purchased from Fisher Scientific Co. Magnesium sulfate heptahydrate was obtained from Mallinckrodt Inc. All reagents were used as received, without further purification. Hydrogen peroxide[13], peracetic acid[14], and other organic peroxides[15] were all analyzed using the cited literature procedures. Analysis of cyclooctadiene has been carried out using a modification of the Mair-Graupner method where the sample is not diluted with additional water prior to the titration.

All optical testing was conducted on handsheets made according to TAPPI standards T-218 and T-205. Brightness was measured according to TAPPI standard T-452, opacity according to T-519. Hunter color parameters are obtained using a Technidyne Brightness Tester and Colorimeter and are calculated from the tristimulous values according to TAPPI standard T-527.

Except where stated otherwise, peracetic acid and peroxide bleaching experiments were carried out in heat sealed Kapak® plastic bags at 20% consistency. Pulp and chemicals were mixed at room temperature in a Hobart® mixer until thoroughly mixed. The pulp was then transferred to a plastic bag which was sealed and placed in a constant temperature hot water bath for the desired length of time.

The *in situ* autoxidation experiments have been carried out in a 55 liter pressure vessel equipped with seven trays, each holding 50 g OD pulp. The trays can be placed in fixed positions on a central shaft fitted in the pressure vessel. Pulp and the vessel were heated to temperature with direct steam prior to adding oxygen.

All other autoxidation reactions were conducted in a 2 liter stainless steel pressure vessel lined with a tall form 600 ml pyrex beaker. The pressure vessel was placed in a stainless steel bucket which was filled with water and heated by a temperature controlled combination hot plate and magnetic stirrer. Reactions were stirred using a teflon coated stirring magnet powered by the magnetic stirrer operating through the stainless bucket and pressure vessel. With cyclooctadiene, some experiments were conducted without solvent by placing several small beakers each with 1 to 2 ml of COD in the same pressure vessel. Because of the smaller volumes, these reactions were not stirred.

Peroxide Bleaching With Molybdenum Trioxide

A large sample of pulp was pretreated with 0.1% DTPA at pH 2.0, 3% consistency, 50° C for 2 hours. The pulp slurry was then filtered and dewatered to 25% consistency to prepare it for high consistency peroxide bleaching. Bleaching was conducted at 20% consistency using 1% hydrogen peroxide, 0.1% MoO_3, 0.1% DTPA, 60° C for three hours. The pH was adjusted in the Hobart® mixer after adding other all other chemicals. Dilute sulfuric acid (or sodium hydroxide) was used to adjust pH. The sample was then transferred to a Kapak® plastic bag. Residual molybdenum analysis were determined by the IPST Analytical Services Group according to EPA.200.7.

Single Stage Peracetic Acid

Pulp was pretreated with 0.05% DTPA at pH 2.0 and 40° C for 60 minutes. Bleaching was carried out using 1% peracetic acid at a starting pH of 8.5 and 20% pulp consistency. The bleach temperature was 40° C with a retention time of 90 minutes. Sodium dihydrogen phosphate was added at a rate of 0.5% on pulp, sodium tripolyphosphate at 0.2% on pulp, and sodium silicate at 3.0% on pulp in their respective experiments. The peroxide control experiment was bleached with 0.5% hydrogen peroxide using 3% silicate and 0.05% magnesium sulfate as stabilizers. Several experiments were performed on pulp that was not pretreated with DTPA. These were less successful and have not been reported.

Two Stage, Peracetic Acid Preceding Hydrogen Peroxide

All samples were pretreated with 0.25% DTPA at pH 2.0 for 1 hour. The peracetic acid stage was conducted using 1% peracetic acid and 0.5% sodium dihydrogenphosphate at 20% consistency, 40° C for 120 minutes. The second stage was carried out with 1% hydrogen peroxide, 3% sodium silicate, 0.05% magnesium sulfate, 180 minutes at 60° C. Bleach consistency in the second stage was approximately 18%. The control was conducted with 1.45% hydrogen peroxide with all other conditions the same as the second stage.

Two Stage Bleaching, Peroxide followed by Peracetic Acid

Samples were pretreated with 0.25% DTPA. First stage is 1% H_2O_2, 3% silicate, 0.05% $MgSO_4$, 20% consistency, 60° C for 90 minutes. Second stage is 1% peracetic acid 10 % consistency, 40° C for 90 minutes. The pulp was not washed between stages but pH was adjusted to 8.5 before adding the peroxyacetic acid.

Oxidation of Sorbic Acid

All reactions were conducted using 1.12 g (10 mmole) of sorbic acid dispersed in 100 ml of solvent using the 2 liter glass line pressure vessel. Peroxide is determined by titration using the modified Mair-Graupner method. The reported yield of peroxide is based on the peroxide concentration in recovered solvent, not total recovery. Yields are the maximum possible yield since in all cases there is some loss of solvent.

In situ Autoxidation of 2,4-hexadienoic Acid

The *in situ* experiments were carried out on a commercial southern pine TMP using the 55 liter pressure vessel and wire mesh trays as described in the general procedures section. All experiments were carried out at 20% consistency, 80° C, 75 psig of oxygen for 90 minutes.

The samples are pretreated with DTPA. Because the experiments were carried out under alkaline conditions, each sample was treated with a conventional peroxide bleach solution to avoid alkaline darkening. This solution contained 2% hydrogen peroxide, 3% silicate and 0.05% magnesium sulfate mixed into the pulp at the same time as the 5% sorbic acid. The conventional peroxide bleach controls were carried out in plastic bags at 20 % consistency, 65° C for 90 minutes.

Oxidation of 1,2,4,5-tetramethyl-1,3-cyclohexadiene

1.3 g (10 mmoles) of 1,2,4,5-tetramethyl-1,3-cyclohexadiene and 0.1 g (1 mmole) of sorbic acid were suspended in 100 ml of water (or 0.1 N NaOH) and transferred to the 2 liter stainless pressure vessel. Several fibers of TMP were added to provide a small amount of lignin as a radical initiator. The pressure vessel was sealed, heated to 65° C and pressurized with 35 psig of oxygen. After 24 hours, the suspension was recovered and analyzed for peroxides using the modified Mair-Graupner procedure. The experiment conducted at pH 9.0 gave a peroxide titration of 0.007 gpl for a peroxide yield of 0.2% from starting material. At pH 12.0, the suspension was titrated at 0.02 gpl for a 0.6% yield from starting material.

Oxidation of 1,5-cyclooctadiene

Approximately 1.39 g (13 mmole) of COD was placed in each of several small beakers and transferred to the 2 liter pressure vessel. These were oxidized at room temperature and 35 psig of oxygen. The reactor was vented at intervals and a sample removed for titration. Samples collected at 1,7,24 and 28 hours were titrated using the standard Mair-Graupner procedure. All gave titrations around 1% conversion to peroxide. Samples collected at 3, 24 and 28 hours were titrated using the modified procedure without water. These gave titrations of 3 to 4% conversion. Using either analysis, the peroxide content of the samples did not vary significantly with time.

CONCLUSIONS/RECOMMENDATIONS

The evaluation of peracetic acid as an alternative peroxide bleaching chemistry indicates that we should not anticipate a significant improvement in molar bleaching efficiency with the alternative peroxides. Attempts to use peracetic acid more selectively as one stage in a two stage bleaching process (with hydrogen peroxide as the other stage) have not shown an advantage over single stage bleaching with equal molar amounts of hydrogen peroxide.

Although autoxidation of butadiene looks promising as a source for cost effective peroxides, we are unable to evaluate it safely at IPST.

Efforts to form other peroxides by autoxidation of readily oxidized organic compounds has failed to give high conversion to peroxides. This is consistent with the literature where high yields of peroxides are often reported based on reacted starting material, but reactions exceeding 10 to 15% conversion are rare. Butadiene, is somewhat unique in this respect because the peroxide separates from the starting material and high conversions are possible.

Autoxidation of 2,4-hexadienoic acid (sorbic acid) gave peroxide products on the order of 5 to 10% yield. No attempt was made to isolate the peroxide. Attempts at *in situ* bleaching with sorbic acid and oxygen were not successful.

Autoxidation of 1,2,4,5-tetramethyl-1,4-cyclohexadiene gave a 1.2% yield of peroxides. This was judged insufficient to warrant further study.

Autoxidation of 1,5-cyclooctadiene gave peroxide yields on the order of 5 to 10%. Analysis of the reaction products by thin layer chromatography shows two principle products, one of which appears to be a peroxide. Attempts to concentrate this material for bleaching studies have not been successful.

FUTURE ACTIVITY

- Additional attempts to concentrate the cyclooctadiene peroxide will be made. It is suspected that the titration results are not an indication of a failure to separate the peroxide from unreacted starting material and alternative analysis will be evaluated. If a COD peroxide can be collected, it will be evaluated for bleaching TMP.

- Linoleic and linolenic acid and their esters are readily oxidized and a solvent extraction procedure exists for isolating the peroxide products. This procedure will be evaluated for obtaining usable quantities of peroxide for bleaching studies.

- The molar bleaching efficiency of *t*-butylperoxide and *t*-butylhydroperoxide will be evaluated. It is expected that the butadiene peroxide will behave more like the dialkyl peroxide and if the bleaching efficiency of the *t*-butylperoxide is low, the project may not be worth pursuing.

- If the peroxides generated from COD or methyl linoleate bleach pulp with reasonable efficiency, and that the *t*-butyl peroxides are also effective, we will seek initiate a cooperative effort to evaluate peroxides from autoxidized butadiene for pulp bleaching.

- Initiate an evaluation of the influence of pH profile on peroxide bleaching.

- Initiate an evaluation of reductive bleaching methods including catalytic hydrogenation.

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PROJECT 3716

ESTIMATING YIELD FOR THE PREDICTIN OF END-USE PROPERTIES IN SEMICHEMICAL PULPING

RESEARCH REVIEW

MARCH 24, 1992

Clark P. Woitkovich and Thomas J. McDonough

Technical Program Review Report

Project Title:	Estimating Yield for the Prediction of End-Use Properties in Semichemical Pulping
Project Staff:	Clark P. Woitkovich and Thomas J. McDonough
Budget (Fy 91-92):	$85,000
Reporting Period:	Jan. '91 - Jan. '92
Division:	Chemical & Biological Sciences
Project No.:	3716

OBJECTIVE:

To identify or develop an analytical test method for the estimation of yield in semichemical pulping and to develop empirical correlations between the analytical test data, estimated yield, and specific end-use properties.

GOAL:

To develop a technology that can be used to improve the control of industrial semichemical pulping processes.

SUMMARY

In the middle- to high-yield range of semichemical pulping, there currently exists no reasonably quick, reliable way of obtaining a quantitative estimate of pulp yield. This project is designed to evaluate several analytical methods that have been determined to be good candidates for this type of application. Several spectroscopic techniques are the most promising of the candidate methods because they possess the greatest potential for on-line application. This report summarizes the progress that has been made in applying these spectroscopic techniques to the analysis of semichemical pulp and liquor samples that have been prepared in the laboratory.

The three spectroscopic methods being investigated are near-infrared (NIR), ultraviolet (UV), and ultraviolet-visible (UV-VIS) fluorescence. To date two of these methods have been applied to lab-generated semichemical liquors and both have exhibited significant yield sensitivity. Sophisticated data analysis approaches have been employed to generate calibrations that can accurately predict yield based on spectral information.

Unfortunately, the value of having a liquor-based yield estimate becomes questionable in light of the fact that many semichemical pulping processes recycle brownstock wash water back to the digester. This complicates the makeup of any given liquor sample and introduces difficulty in attempting to relate that liquor sample to a specific pulp sample. Consequently, it is recommended that liquor analysis be abandoned as a potential yield estimation method and that all future efforts focus exclusively on the analysis of pulp.

The NIR spectroscopic technique is the only pulp analysis method that has exhibited yield sensitivity in the laboratory. However, the small size of our laboratory sample set has not allowed for a rigorous test of the predictive capability of this method. Future work will focus on the development of more robust calibrations and then testing the performance of these calibrations in actual mill environments.

INTRODUCTION

Knowledge of the yield associated with a chemical reaction is critical if raw materials are to be utilized with maximum efficiency. In the pulping of wood, yield is defined as:

$$\% \ Yield = \frac{pulp\ weight\ X\ pulp\ consistency}{wood\ weight\ X\ wood\ consistency} \ X\ 100$$

In industry, the pulping process is generally conducted on such a large scale that it is nearly impossible to accurately measure the parameters that determine yield. Consequently, yield becomes an elusive quantity that can only be estimated through some indirect approach.

Typically, such an approach is based on an analysis of pulp lignin content (e.g. "Klason" lignin or kappa number). Lignin content analyses, however, generally suffer several drawbacks. They are destructive, time-consuming, wet-chemical tests that require skilled laboratory personnel. Another problem is that these analyses ignore the carbohydrate fraction in pulp and its contribution to a yield estimation. Furthermore, kappa number, the most routinely used lignin content test, is limited in its range of applicability and becomes virtually useless when lignin content is high, as is the case with semi-chemical pulps.

Consequently, in the middle- to high-yield range of semichemical pulping there exists no reasonably quick, reliable way of obtaining a quantitative estimate of yield. If such a capability were to be achieved it would become possible to monitor yield regularly, or perhaps even continuously. Yield could thus be used as a process control parameter, making it possible to more effectively control the pulping reaction, and thereby, the development of pulp properties.

Several analytical methods have been determined to be good candidates for this type of application and are being applied to pulps and/or liquors as indicated in Table 1. A brief background on the spectroscopic techniques is presented as follows; for a more detailed discussion of these methods, the reader is referred to the preceeding report (1).

Table 1: Candidate Yield Estimation Techniques

	PULP	LIQUOR
SPECTROSCOPIC METHODS	Near-Infrared Reflectance	Near-Infrared Transmittance
	Ultraviolet-Visible Luminescence	
	Ultraviolet-Visible Reflectance	Ultraviolet-Visible Transmittance
OTHER	-	Refractive Index
	-	Total Organic Carbon
	-	Total Dissolved Solids
	Hypo Number	-

Near-infrared Absorbance Spectroscopy

The near-infrared (NIR) absorption characteristics of pulp samples are readily measured by monitoring the intensity of reflected radiation as incident wavelength is varied. In the case of liquor samples, the measurement is based on transmitted rather than reflected radiation. The resultant data is a plot of absorbance as a function of wavelength and is called an absorbance spectrum.

NIR spectra consist primarily of overlapping bands that result in broad spectral features from which it is difficult to derive structural information. The spectra, however, have been found to be empirically useful in a variety of quantitative analysis applications. The appeal of NIR spectroscopy (NIRS) lies in its fast analysis time, its minimal sample preparation requirement, its relatively compact and rugged design, and its recently emerged compatibility with fiber optic technologies. These attributes have rendered NIRS an ideal candidate for several on-line applications in the pulp and paper industry.

Ultraviolet-Visible Fluorescence Spectroscopy

The fluorescence phenomenon is observed when a substance, excited by incident light radiation, dissipates some of its excitation energy in the form of emitted light. With suitable instrumentation three distinctly different records of fluorescence behavior can be acquired; excitation spectra, emission spectra and synchronous spectra. Excitation spectra arise when the intensity of the fluorescence is monitored, at a specific emission frequency, while continuously varying the excitation frequency. Conversely, the excitation frequency can be held constant while the intensity of the fluorescence is monitored over a wide range of emission wavelengths. This results in what is known as a fluorescence emission spectrum. Finally, there is the capability of simultaneously varying both excitation and emission wavelength settings, at a fixed wavelength separation, to generate a synchronously scanned, or "fingerprint" fluorescence spectrum.

As in the case of NIR spectra, fluorescence spectra exhibit primarily broad spectral features that tend to confine data interpretation to an empirical level. On the other hand, all of the same attributes that have rendered NIRS an ideal candidate for potential on-line applicability also hold true for fluorescence spectroscopy. Although the method does not seem to share the increasingly widespread industrial acceptance enjoyed by NIRS, its attributes warrant that it be included in this study.

Ultraviolet-Visible Absorbance Spectroscopy

The measurement of UV-VIS absorbance involves essentially the same approach as that used in the measurement of NIR absorbance; the only difference is in the wavelength range that is used. The technique, as applied to liquid samples, is a commonplace analytical tool that has proven useful in the routine measurement of solution concentration. As applied to non-homogeneous solids, the method is far less developed.

In this study, a somewhat novel approach was taken to the measurement of the UV-VIS absorbance characteristics of pulp. Spectra were recorded by operating the scanning UV-VIS fluorescence spectrometer in a mode that had the excitation wavelength and the emission wavelength set to the same value.

Sample Preparation

The set of samples used throughout this portion of the project was prepared in the laboratory by cooking chestnut oak chips, under neutral sulfite semichemical (NSSC) conditions, to eight different yield levels that varied over the range of 74.7% to 84.0%. Cooked chips exiting the digester were extensively washed and then fiberized for 15 minutes in a Waring blender. Following the fiberization step, the pulp underwent further washing and was then pressed to a common consistency before being mechanically fluffed. Liquor samples received no treatment other than a dilution (1:100) prior to the UV-VIS fluorescence and UV-VIS absorbance measurements.

REVIEW OF PAST PROJECT ACTIVITY

In the previous progress report presented to this body, we reported our earliest observations of spectroscopic differences that were apparently yield-related (1). Specifically, significant differences were shown to exist in the transformed NIR absorbance spectra recorded from a subset of the laboratory pulps that had been cooked under semichemical conditions to different yields. This early work included experiments designed to study the effect of sample form on spectral data. It was found that the above-mentioned spectral differences were consistently exhibited to varying degrees, in all three of the investigated sample forms: moist fluff, dry fluff, and dried sheet. The most pronounced differences were observed in the case of the dried sheets. If samples were presented in a fluffed form that still contained an appreciable amount of moisture, spectral differences were reduced. The differences remained significant, however, and were thought to justify the elimination of a drying step in the sample preparation procedure, thereby simplifying the NIRS analysis.

Spectral differences were also evident in the UV-VIS fluorescence excitation spectra acquired from the same pulp samples. At that time, the fluorescence technique had been applied only to fluffed pulp and no conclusions could be made regarding the effect of sample form on these measurements. There was an indication, however, that the technique might not be suitable for wet pulp analysis.

Since these findings, our research efforts have continued to focus exclusively on the spectroscopic techniques. Using an expanded sample set, we set out to explore factors that were critical to the development of yield sensitivity in a given method. Specifically, there was a need to further understand the effects of not only yield, and sample form, but also moisture content, and sample presentation on the spectral data

acquired by the various methods. In addition, in the case of the fluorescence work, it was necessary to investigate a variety of data acquisition and data analysis options. This report addresses the progress that has been made in these key areas.

DISCUSSION OF 1991 RESULTS:

NIR Spectroscopy as Applied to NSSC Pulps

Since pulp NIR spectra exhibited apparent yield-related differences even when the pulps were wet, it was decided to work exclusively with wet pulps. Wet pulp is, after all, what is likely to be encountered in an eventual on-line implementation of this technology.

Our efforts in this area were divided into essentially two sets of experiments. The first set of experiments focused on only two pulp samples from our original eight-sample set so that the method could be further optimized before analyzing the entire number of samples. The two samples, representing the extremes of our known yield range, were first brought to a consistency of 30-35% and then analyzed repeatedly in fluffed and unfluffed form using two different types of sample presentation cell. The objective was to quantify the effects of sample form and sample cell type on the discriminatory power of the method. The discriminatory power can be thought of as an indicator of yield sensitivity and is dictated by the relationship between the magnitude of the observed spectral differences and the magnitude of the measurement variability.

Figure 1 shows raw NIR spectra acquired from the two different high yield pulp samples. One sample was a pulp that was cooked to a yield of 82.7% and the other was a pulp cooked to a 74.7% yield. These two representative absorbance spectra illustrate the types of differences that are observed in the raw data acquired from wet samples that differ significantly in yield. One noticeable difference resides in the intensities at the two very strong absorption bands centered at approximately 1490 and 1950 nm. These bands are water absorption bands and their intensity differences probably arise from slight differences in consistency between the two samples. Although potentially useful for the estimations of pulp consistency, the regions of the spectrum where these bands appear must be avoided when developing correlations between spectral features and yield.

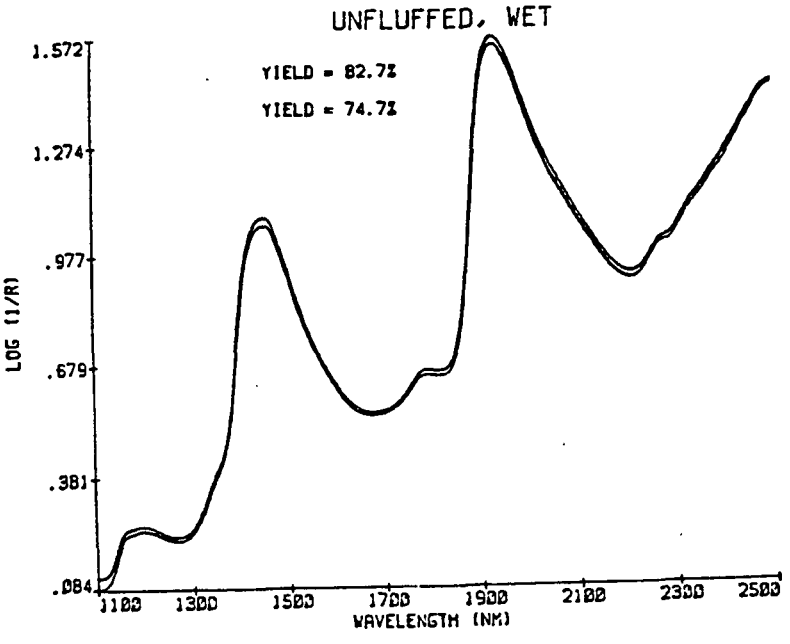

Figure 1. Raw NIR absorbance spectra acquired from two different high yield pulp samples at a consistency of approximately 30-35%.

The other important difference between the spectra in Figure 1 is the vertical offset or base line shift that is observed throughout most of the acquisition range. Base line shift is primarily a surface scattering effect. It can be caused, at least in part, by a variety of sampling-related factors, such as particle size distribution, packing density, and other sample surface properties. In order to focus on spectral differences that are not influenced by surface related effects, it is essential to compensate for base line differences. A convenient way of accomplishing this is to mathematically transform raw spectral data into second derivative spectra. The conversion of spectra to their second derivatives compensates for these factors by combining displaced or sloping base lines into a common, horizontal base line.

Second derivative spectra were calculated using raw data acquired from wet, fluffed and unfluffed pulps that were presented for analysis in the two different sample cells. A select region of the derivative spectra, known to be devoid of water absorption bands (1580-1750 nm), is shown in Figure 2. In each of the four separate plots, four spectra representing four different reloads, are shown for each sample. The most prominent difference between samples occurs at approximately 1638 nm, a region where lignin is known to absorb. The yield sensitivity or discriminatory power, of each presentation condition was quantified by performing a two sample t-test on the measured intensity at 1638 nm (Table 2).

Table 2. t-values representing the relative discriminatory power of indicated presentation conditions. Values were calculated on measured intensities at 1638 nm.

	CUP	TRANSPORT
UNFLUFFED	4.1	11.0
FLUFFED	5.7	38.1

Note: A t-value greater than 2.8 indicates that the two pulps can be said to differ in yield with a 95% probability of being correct. The higher the t-value, the greater is the probability of correctness of this statement, and the greater is the ability of the measurement method to detect a yield difference of any given magnitude.

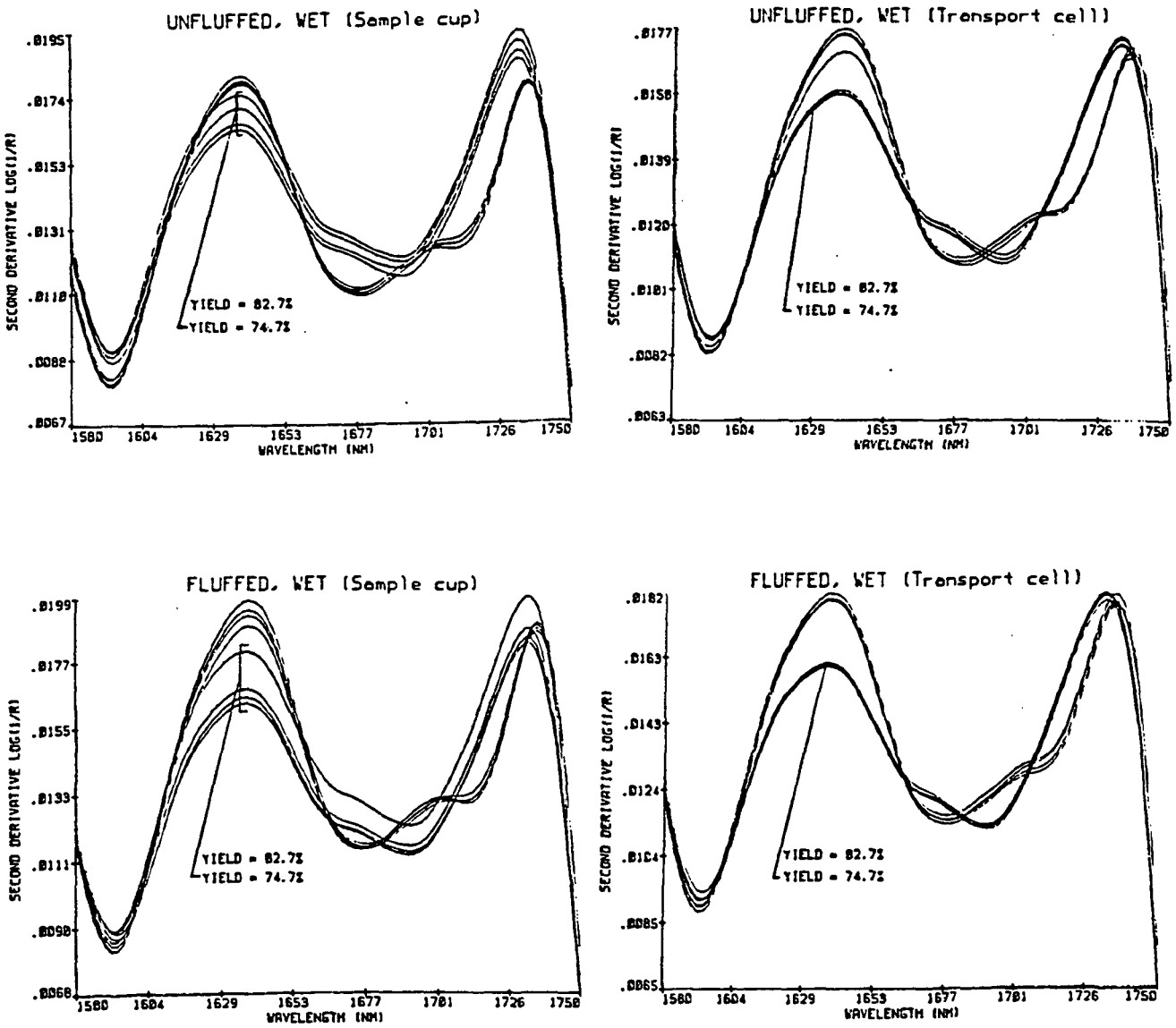

Figure 2. Low frequency region of second derivative NIR absorbance spectra acquired from fluffed and unfluffed pulps in two different sample cells.

The results summarized in Table 2 indicate that, at 1638 nm, the highest discriminatory power (or lowest reload variability) is achieved when pulps are presented in fluffed form using the transportable cell. This finding is not surprising because, under these conditions, both analyzed surface area and surface homogeneity are maximized. What is surprising is the magnitude of the improvement that can be made by optimizing sample presentation.

In summary, two important findings have emerged from this set of NIRS experiments:

1) the transportable sample cell is the superior sample presentation device for the NIRS reflectance analysis of pulp, and

2) excellent yield discriminatory power is achievable without the necessity of sample drying.

The NIRS method appears to be relatively unconstrained by elaborate sample preparation requirements, thus enhancing its potential applicability to on-line analysis.

The second set of NIRS experiments mentioned above focused on acquiring a series of spectra from the entire pulp sample set. In this case, the analyses were performed at a pulp consistency of approximately 16.5% to more closely simulate the type of analysis that would be done in the mill on pulp exiting a brownstock washer. Figure 3 shows representative raw NIR spectra acquired from two high-yield pulps (74.7 and 84.0%) at 16.5% consistency. The spectra illustrate the dominance of water absorption bands and the apparent subtlety of yield-related differences, if they even exist. A comparison of Figures 1 and 3 reveals the effect that a significantly higher moisture content has on raw spectral data.

After second derivative transformation and expansion on the wavelength axis, the set of spectra is seen to exhibit significant differences that correlate closely with gravimetric yield values (Figure 4). The overall appearance of these spectral differences, however, when compared to those observed in Figure 2, seems to be significantly affected by the changed pulp moisture content. The yield-related differences appear to be reduced in magnitude and confined to a smaller wavelength range.

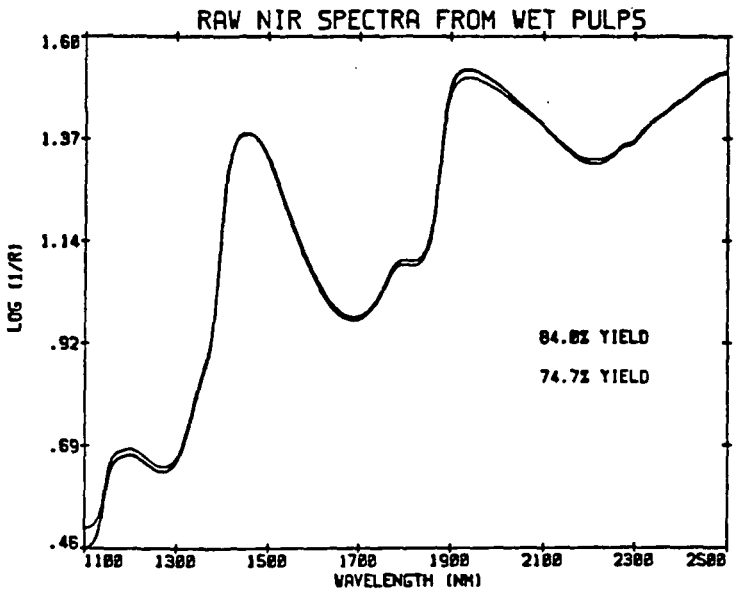

Figure 3. Raw NIR spectra acquired from two different high-yield pulp samples at a consistency of approximately 16.5%.

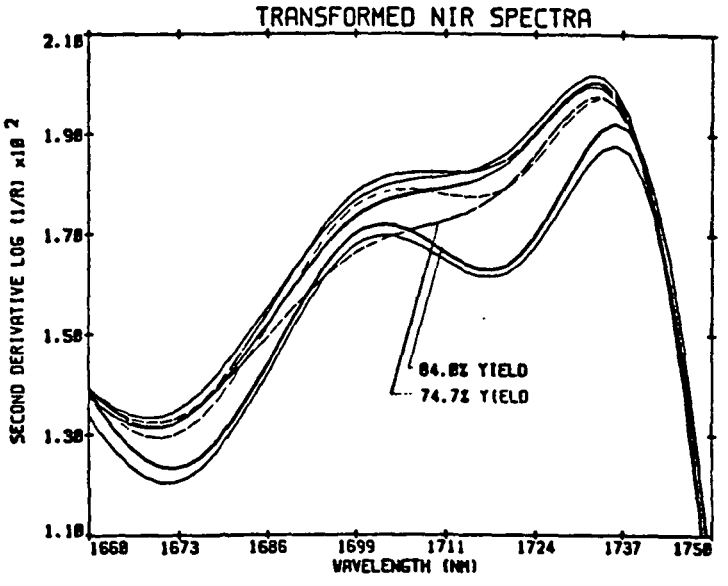

Figure 4. Selected region of NIR spectra acquired from wet (16.5% consistency) pulps obtained by cooking chestnut oak, under NSSC conditions, to a variety of yields ranging between 74.7% and 84.0%. Spectral data is shown after second derivative transformation and wavelength scale expansion.

A plot of gravimetric yield vs. predicted yield is shown in Figure 5. Predicted yield values were generated using a Partial Least-Squares cross validation (PLS-CV) algorithm (2,3) that is resident in the NIRS software.

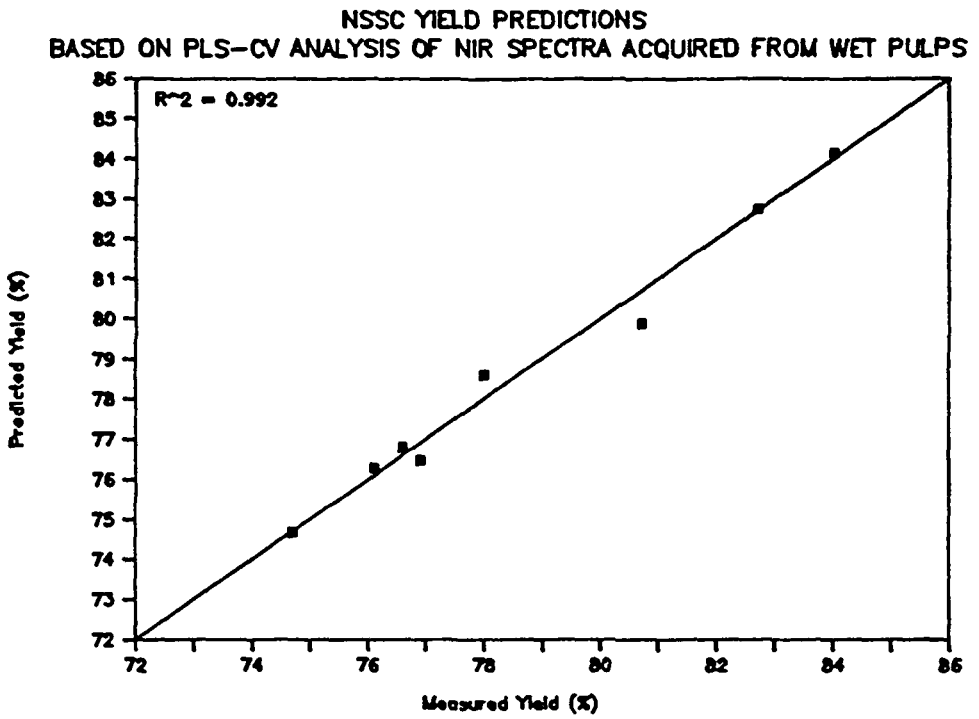

Figure 5. Plot of measured vs. predicted yield. Predicted yield values were generated using the calibration developed by PLS-CV analysis of spectra acquired from the eight wet pulp samples that varied in yield from 74.7% to 84.0%.

The conclusions drawn from this second set of NIRS experiments are:

1) Decreasing pulp consistency (to a level that might be encountered on a brownstock washer) results in a significant reduction in the magnitude of yield-related spectral differences, and

2) Yet, sophisticated calibration algorithms are still capable of generating accurate yield predictions based on the NIR spectral data acquired from low consistency (16.5%) pulps.

UV-VIS Fluorescence Spectroscopy as Applied to NSSC Liquor

At the outset, it was not known which, if any, of the three possible fluorescence acquisition modes would prove to be most informative. Therefore, it seemed wise to investigate all three of these capabilities in an effort to develop a complete characterization of liquor fluorescence behavior. Unfortunately, for each acquisition mode, there were literally dozens of possible wavelength settings. Consequently, a fairly exhaustive preliminary investigation was required in order to identify those wavelength settings that were optimal for subsequent quantitative analysis.

By analyzing a single liquor sample in all of the different acquisition modes, it was found that the choice of wavelength settings significantly influenced either the overall signal intensity, the shape of prominent spectral features, or both. This information was used to identify what appeared to be the most informative settings in each mode before beginning the analysis of liquor samples that represented different pulp yield levels.

Additional preliminary spectra were acquired, using the selected settings, in an effort to ascertain: a) whether liquors associated with widely different yield levels would generate significant spectral differences, and b) whether the magnitude of measurement variability was sufficiently small relative to observed yield-related spectral differences. Unless both these conditions were met, it would not be possible to develop correlations between pulp yield and liquor fluorescence. What was concluded was that, under all of the selected acquisition conditions, significant yield-related differences were evident. Specifically, in the case of both the excitation and synchronous spectra, yield-related differences appeared in the form of dramatic changes in the relative intensities of prominent spectral features.

Ultimately, the entire laboratory series of eight different NSSC liquors was analyzed using six selected acquisition conditions (i.e., two different wavelength settings for each of the three acquisition modes). Two of the six complete data sets, comprised of eight spectra each, are shown in Figure 6. Each spectrum displayed represents a computed average spectrum derived from duplicate acquisitions.

The representative data shown in Figure 6 consists of two series of spectra acquired in the excitation mode, one set (6a) was recorded with the emission wavelength set to 470 nm, and the other (6b) with it set to 530 nm. For display purposes, each spectrum in Figures 6a and 6b was multiplied, over its entire range, by a factor chosen to give a constant intensity at approximately 395 nm. One observation that is immediately apparent in Figure 6 is that fluorescence spectroscopy, as applied to NSSC liquors, is evidently highly sensitive to variations in liquor composition that are associated with pulp yield differences (74.7-84.0%). Spectral features appear to vary in a regular fashion.

The apparent abundance of information in full-range fluorescence spectra, including the observed yield sensitivity, is presumed to reflect the overall chemical characteristics of the liquor samples. The implication is that both dissolved carbohydrate fragments and dissolved lignin fragments contribute to the measured fluorescence. This is important from the standpoint of our objective because no yield-estimation method can be considered reliable unless it is based on an analysis that reflects information related to both the lignin and carbohydrate fractions of the analyte.

Identification of an optimum quantitative analysis approach required an intensive investigation of several different normalization and calibration methods. The simplest normalization approach was a base line subtraction procedure. Performing this type of normalization and measuring the ratioed intensities of prominent spectral features generated a strong linear correlation between the spectral data and known gravimetric yield ($R^2 = 0.896$). The use of more sophisticated normalization and calibration procedures, i.e. Multiplicative Scattering Correction (4) and PLS-CV, demonstrated that the fluorescence data can be used to accurately predict yield, as seen in Figure 7.

One early indication to come out of this fluorescence work was that the shape of a fluorescence spectrum did not appear to be affected by changes in sample concentration. Spectral information believed pertinent to yield prediction was reported to be retained up to a point where dilution becomes excessively high (resulting in an unacceptable signal-to-noise ratio). It turns out, however, that after more careful scrutiny, this conclusion proved not to be entirely correct. Spectral features

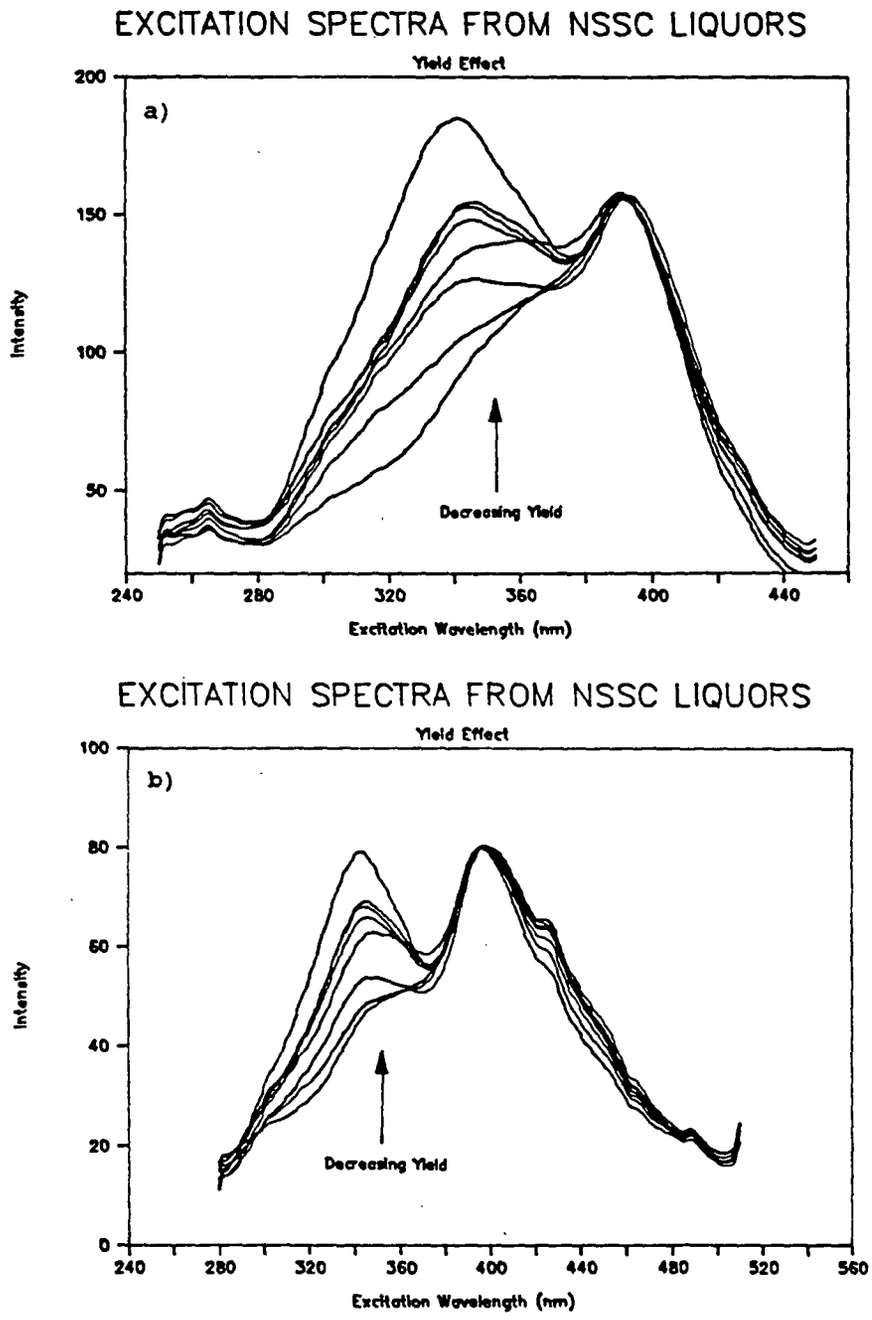

Figure 6. Fluorescence excitation spectra acquired from diluted (1:100) spent semi-chemical pulping liquor obtained by cooking chestnut oak under NSSC conditions, to a variety of yields ranging between 74.7% and 84.0%. Spectra in 6a were recorded at Em_λ = 470 nm; in 6b Em_λ = 530 nm.

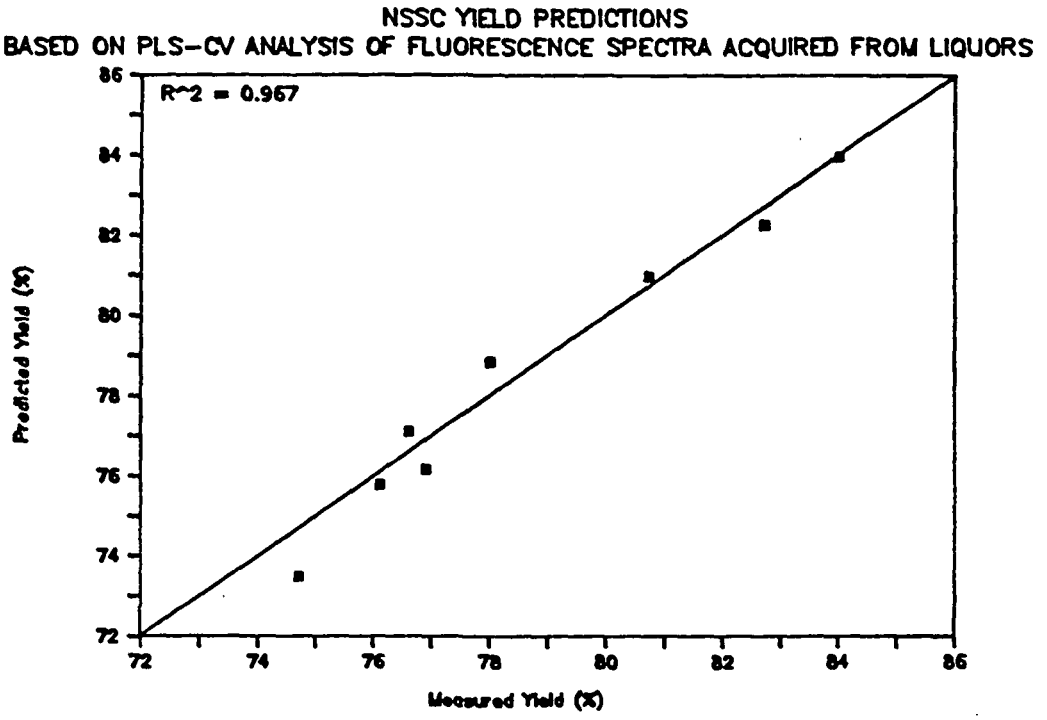

Figure 7. Plot of measured vs. predicted yield values. Pretreated yield values were generated by performing a PCS-CV analysis of fluorescence excitation spectra acquired from the eight liquor samples representing a pulp yield range of 74.7 to 84.0%.

are indeed affected by liquor concentration levels in a way that will interfer with fluorescence-based yield estimation. The magnitude of the interference is fairly subtle, however, which is why it escaped detection earlier. Current efforts are exploring the development of potential correction methods designed to compensate for these unwanted concentration effects. Some measurable success has already been achieved.

UV-VIS Fluorescence Spectroscopy as Applied to NSSC Pulps

The characteristic fluorescence behavior of one particular semichemical pulp sample (82.7% yield) was recorded in the excitation, emission, and synchronous scan acquisition modes over a wide range of wavelength settings. The wavelength settings that produced the most dramatic spectral features were adopted in subsequent fluorescence experiments that focused on detecting possible yield-related spectral differences.

Although apparently significant differences were found, the potential usefulness of the observed differences was ultimately undermined by the degree of variability associated with the acquisition of each spectrum (i.e. reload variability). Such variability is shown in Figure 8, along with the effect of moisture content on overall spectral features. Reload variability appears to be substantial, approaching, in several cases, the magnitude of the differences that are apparently related to yield. It is also obvious that increasing moisture content causes a drastic reduction in the overall intensity of the detected fluorescence. For these reasons, it was decided to abandon further pursuit of the UV-VIS fluorescence method as applied to pulp, especially in light of the relative success achieved with the NIRS method.

Perhaps the most significant reason behind the failure of fluorescence spectroscopy, as applied to pulp, is that there is no sample presentation accessory that allows for the averaging of spectral information from a large sample area. As seen with the NIRS data, this capability is crucial when analyzing the optical phenomena of non-homogeneous materials, such as pulp.

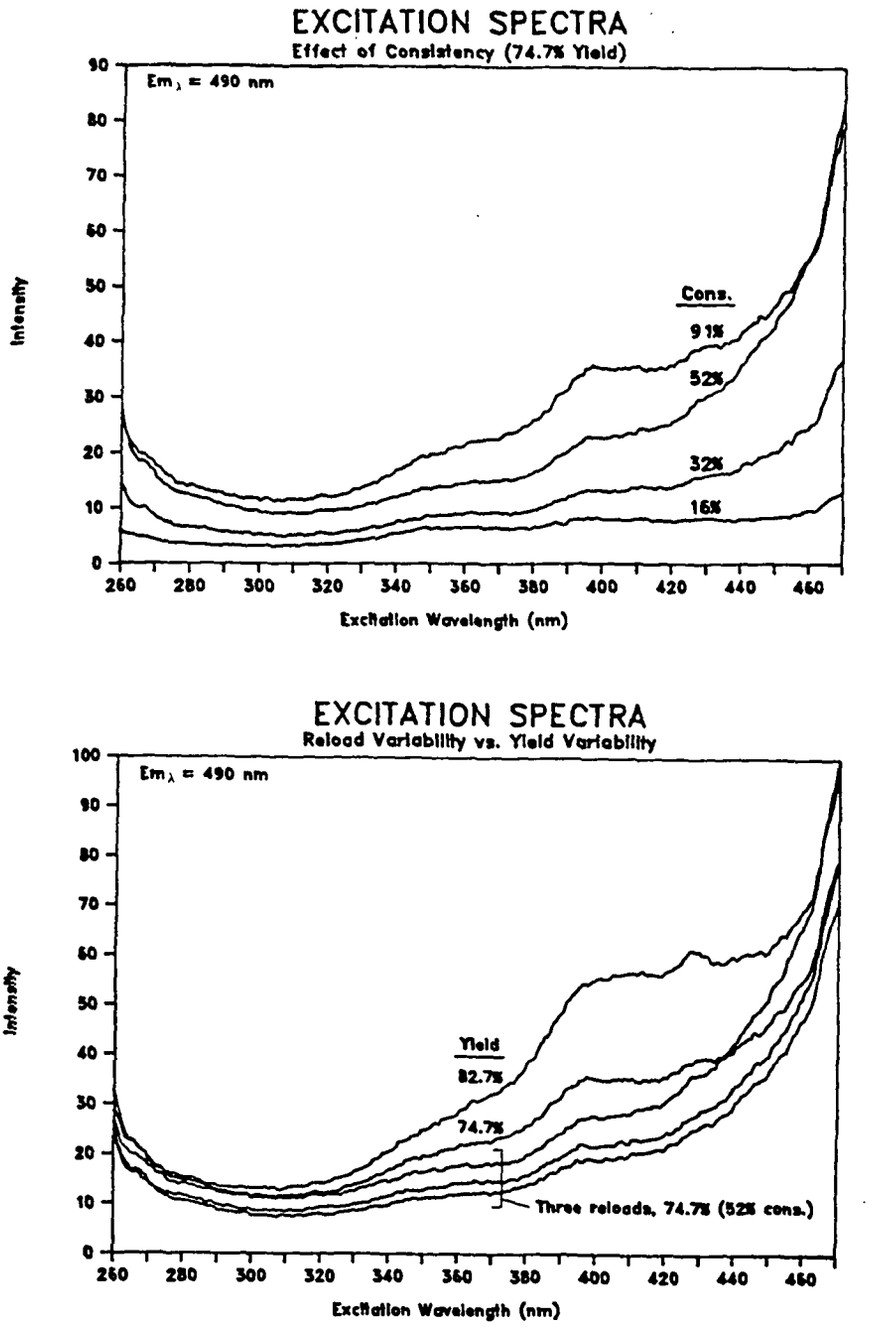

Figure 8. Fluorescence excitation spectra showing the effect of consistency and a comparison of reload variability vs. the magnitude of apparent yield-related differences.

UV-VIS Absorbance Spectroscopy as Applied to NSSC Pulp

Raw UV-VIS reflectance spectra were acquired from two air-dried, fluffed pulp samples that possessed different yield levels. Figure 9 shows the reflectance spectra obtained when excitation and emission wavelength settings were synchronously scanned over the ranges 230-350 nm and 350-650 nm. It was necessary to scan the overall wavelength range in two separate parts because a reduction in signal attenuation was required in order to detect the extremely low reflectance in the UV region.

In the UV and UV-VIS reflectance plots, each yield level is represented by six individual spectra acquired from six different sample reloads. It is readily apparent from Figure 9 that, in both wavelength regions, there is considerable overlap of the ranges of reload variability for each sample. Apparently, it is not possible to obtain acceptable measurement reproducibility with our present capabilities. Since the UV-VIS absorbance of pulps was measured using the fluorescence spectrometer, the explanation for this finding can be traced back to the above-mentioned instrumental drawback.

UV Absorbance Spectroscopy as Applied to NSSC Liquor

Figure 10 shows UV absorbance spectra acquired from the eight NSSC liquor samples described earlier. As in the case of the fluorescence spectra, UV absorbance spectra appear to be sensitive to apparent variations in liquor composition that are associated with yield differences. Two prominent absorption bands are immediately evident: one appears in the 255 to 260 nm range; the other at approximately 275 to 280 nm.

Difficulties in data downloading with this instrument prohibited us from employing the more sophisticated PLS-CV approach to the development of a yield correlation. Thus, we opted for a simple linear regression analysis using a single peak intensity (I_{275}) or ratio of intensities (I_{275}/I_{255}). These values are tabulated with the gravimetric yields in Table 7. The R^2 values indicate the existance of moderately strong correlations between the UV absorbance data and known yield levels. Further work is necessary, however, to assess the reproducibility of these measurements and to examine the impact of liquor concentration on the appearance of pertinent spectral features.

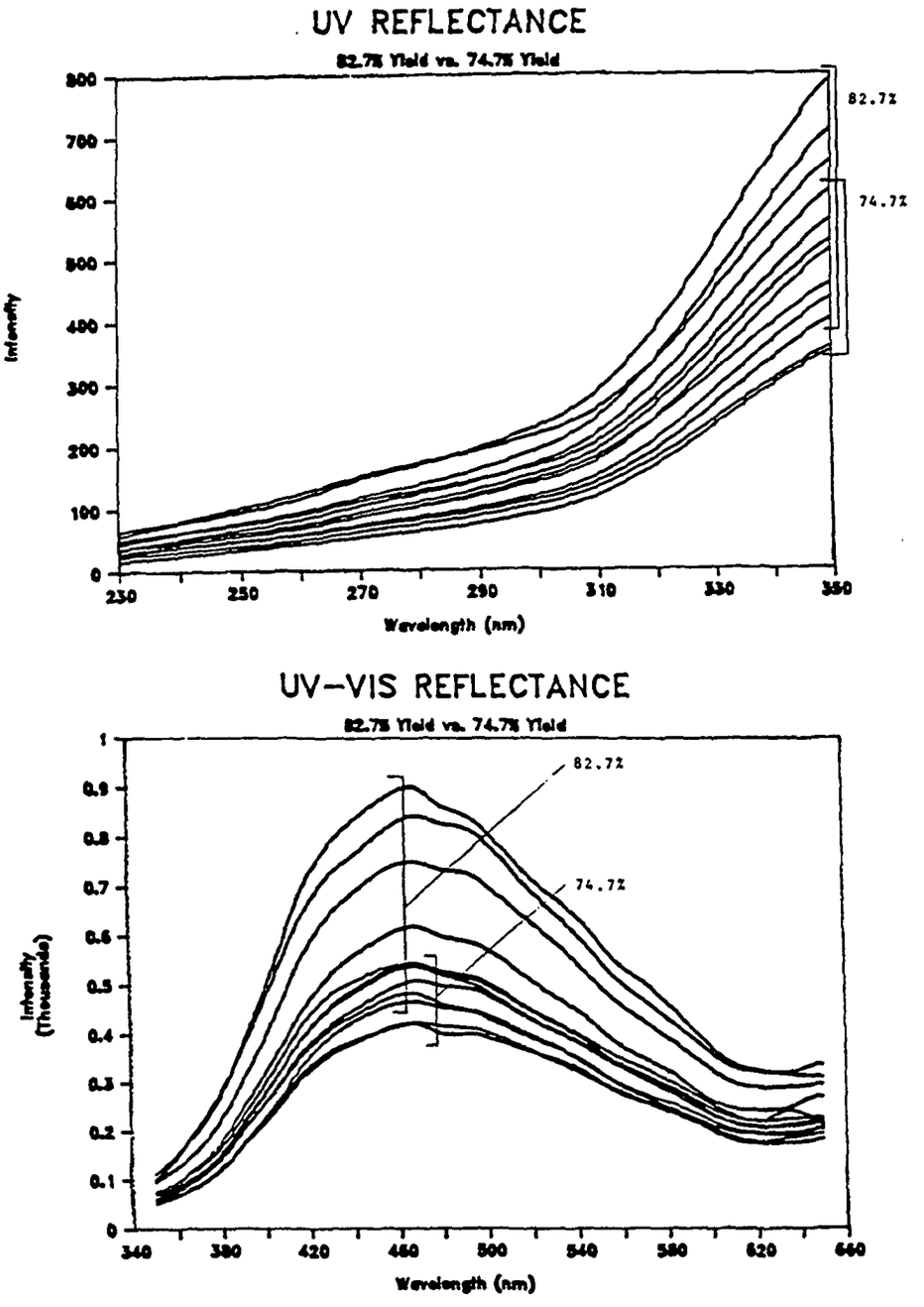

Figure 9. Raw UV-VIS reflectance spectra acquired from two air-dried, fluffed pulp samples having different yield levels. Each sample was reloaded and reanalyzed six times.

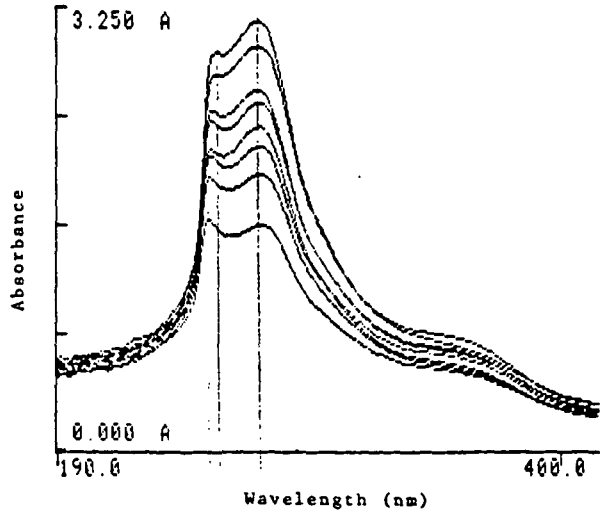

Figure 10. Ultraviolet absorption spectra acquired from diluted (1:100) spent semi-chemical pulping liquor attained by cooking chestnut oak, under NSSC condition, to a variety of yield levels ranging between 74.7 and 84.0%.

Table 7. Intensities and ratioed intensities of selected ultraviolet absorption bands.

Yield, %	I_{274}	$I_{274}/I_{254\text{-}258}$
84.0	10.85	0.977
82.7	13.22	1.011
80.7	14.52	1.035
78.0	16.06	1.022
76.9	19.25	1.077
76.6	15.47	1.072
76.1	17.12	1.057
74.7	20.45	1.082
	$R^2 = 0.830$	$R^2 = 0.832$

CONCLUSIONS AND RECOMMENDATIONS

The two spectroscopic methods that have been applied to the analysis of lab-generated semichemical liquors have both exhibited significant yield sensitivity. Sophisticated data analysis approaches have generated calibrations that can accurately predict yield based on spectral information.

The value of having a liquor-based yield estimate becomes questionable, however, in light of the fact that many semichemical pulping processes recycle brownstock wash water back to the digester. This complicates the makeup of any given liquor sample and introduces difficulty in attempting to relate that liquor sample to a specific pulp sample. Consequently, it is recommended that liquor analysis be abandoned as a potential yield estimation method and that all future efforts focus exclusively on the analysis of pulp.

Investigations of the various spectroscopic methods, as applied to pulps, has shown that the NIR technique is the only pulp analysis method that has exhibited yield sensitivity in the laboratory.

FUTURE WORK

As recommended, all future work on this project will focus exclusively on the NIR spectroscopic analysis of pulp. The technique will undergo mill evaluations that are designed to test its performance under the daily rigors of plant operation. Prior to the initiation of any mill trial, further laboratory work will be conducted to develop a statistically sound, workable calibration to be used for yield prediction while on-site. To enhance the applicability of the laboratory calibration to mill data, considerable attention will be devoted to the careful simulation of mill pulping conditions.

A wet chemical laboratory analysis designed to quantify the major chemical constituents of pulp, i.e. cellulose, hemicellulose, and lignin, will be used as a backup analytical test to verify that spectral measurements in the mill actually reflect real yield variations. Such an analysis will also add to our knowledge concerning the fundamental reasons behind the observation of yield-related spectroscopic differences.

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PROJECT 3701

AN EVALUATION OF SODIUM CARBONATE AS A REPLACEMENT FOR SODIUM HYDROXIDE IN HYDROGEN PEROXIDE BLEACHING OF CTMP

RESEARCH REVIEW

MARCH 24, 1992

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Technical Program Review Report

PROJECT TITLE: Evaluation of Na_2CO_3 as Alkali in Peroxide Bleaching of CTMP

PROJECT STAFF: A. W. Rudie, T. J. McDonough

BUDGET: Contract, FMC Corporation

REPORTING PERIOD: July '91 - January '92

DIVISION: Chemical and Biological Sciences Division

PROJECT NUMBER: 3701

OBJECTIVE:

Evaluate the use of sodium carbonate as a source of alkali in peroxide bleaching of high yield pulps.

GOAL:

Determine whether sodium carbonate can be used to replace all or part of the sodium hydroxide required in peroxide bleaching of spruce CTMP.

SUMMARY:

An extended series of laboratory bleaching experiments was performed to evaluate the effects of substituting sodium carbonate (soda ash) for the sodium hydroxide generally used in peroxide bleaching of high yield pulps. A commercial sample of spruce chemithermomechanical pulp (CTMP) was bleached using three levels of peroxide, (1, 2, and 4% on OD pulp). The caustic charge was varied to determine the appropriate charge to maximize brightness gain. The optimum caustic charge at the 2%, and 4% peroxide levels was then reduced by 50% and 80% and sodium carbonate added to supplement the sodium hydroxide.

Table 1: Summary Optimum Predicted Brightness

% H_2O_2	% NaOH	% Na_2CO_3	Brightness
2%	2.6	0	71.2
2	1.3	0.5	70.7
2	0.5	1.7	70.3
4	4.3	0	75.2
4	2.2	1.9	74.2
4	0.9	5.7	73.8
2.3	1.3	0.8	71.2
4.8	2.2	3.6	75.2

Starting GE brightness, 61.1

The results of the peroxide bleaching experiments were used to develop a mathematical model for peroxide bleaching using sodium hydroxide and sodium carbonate as alkali. Summary results from the model are given in Table 1.

Referring to the model results in Table 1, at the 2% peroxide level, peak brightness is 71.2 GE, (10 points brightness gain) obtained using sodium hydroxide as the source of alkali. Reducing the sodium hydroxide charge from 2.6% to 1.3%, and making up the alkali with sodium carbonate results in a maximum brightness of 70.7 GE, a loss of 1/2 point in brightness. Reducing the sodium hydroxide charge by 80% to 0.5% on OD pulp results in an additional decrease in maximum brightness to 70.3 GE, a total loss of 0.9 points relative to the control. The sodium carbonate charge required to obtain the maximum brightness is quite low in both cases with substitution ratios of 0.4 grams Na_2CO_3 per gram NaOH for the 50% replacement case, and 0.9 grams carbonate per gram NaOH in the 80% replacement alternative.

At the 4% peroxide level, maximum brightness gain is 14 points to 75.2 GE. Again, maximum brightness is obtained with sodium hydroxide as the source of alkali. Replacing 50% of the sodium hydroxide with carbonate results in a loss of 1 point in brightness to 74.2 GE. Replacing 80% of the caustic reduces the maximum achievable brightness to 73.8 for a total loss of 1.4 points relative to the sodium hydroxide control case. Caustic substitution ratios are 0.9 and 1.7 grams carbonate per gram of caustic for the 50% and 80% replacement options respectively.

The mathematical model has been used to estimate the hydrogen peroxide charge required to maintain brightness when reducing the sodium hydroxide charge by 50%. These estimates are also summarized in Table 1. At the 10 point brightness gain level, reducing the sodium

hydroxide applied by 50% requires an increase in the peroxide charge from 2% to 2.3% on OD pulp. At the 14 point brightness gain level, the increased required is from 4% to 4.8% peroxide on pulp. The sodium carbonate requirement also increases in both cases.

Handsheets were made from six selected pulp samples bleached under conditions maximizing the brightness gain. Physical testing of these handsheets indicates a 5 to 15% loss in Tensile Index when using sodium carbonate to supplement the caustic charge. No change is observed in Tear Index and Burst Index. These results are reported in Table 6.

Ambient and light reverted brightness tests were also made on these six samples. The results indicate an improvement in brightness stability for samples bleached using a mixture of sodium hydroxide and sodium carbonate as alkali. In the 2% peroxide case, the samples bleached using the mixed alkali exhibit higher brightness after reversion than the caustic control experiment. These results are reported in Table 7.

AN EVALUATION OF SODIUM CARBONATE AS A REPLACEMENT FOR SODIUM HYDROXIDE IN HYDROGEN PEROXIDE BLEACHING OF CTMP

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Abstract: A series of experiments was performed to evaluate the effect of substituting sodium carbonate (soda ash) for the sodium hydroxide used in peroxide bleaching of spruce CTMP. Three peroxide levels were tested: 1, 2, and 4% H_2O_2 (OD basis) and two levels of caustic substitution, 50% and 80%. At both the 2% and 4% peroxide levels, substituting 50% of the caustic charge with soda ash decreased the initial brightness gain by 1 point in TAPPI brightness. At the 80% caustic substitution level, the brightness gain decreased 1.5 points. Use of sodium carbonate as part of the alkali source in the bleaching process reduces the sensitivity of final bleached brightness to the alkali charge and should result in improved control. In all cases, soda ash substitution was found to improve brightness stability, and in some cases, ash substituted samples gave higher reverted brightness than the caustic control. A mathematical model was developed to describe peroxide bleaching with both sodium hydroxide and sodium carbonate as sources of alkali. Handsheets were made from selected pulp samples. Tear Index and Burst Index were unaffected by ash substitution. Tensile Index was reduced 5 to 15%.

Résumé: Une série d'expérience fut effectuée afin d'évaluer l'effet de la substitution de l'hydroxyde de sodium (soude caustique) par le carbonate de soude dans le blanchiment au péroxyde d'hydrogéne de la pâte PTCM (épinette). Trois niveaux de dosage de péroxyde furent analysés: 1, 2 et 4% H_2O_2 (base anhydre) et deux niveaux de substitution de soude caustique, soit 50 et 80%. Au deux niveaux de 2 et 4% de péroxyde et en remplaçant 50% de la charge de soude caustique par le carbonate de soude, le degré de blancheur initiale fut réduit de 1 point (échelle de TAPPI). En remplaçant la soude à 80%, le degré de blancheur fut réduit de 1.5 point. L'utilisation du carbonate de soude comme portion de la source d'alcali dans le procédé de blanchiment réduit la sensibilité du degré de blancheur finale à la charge d'alcali et devrait conduire à une amélioration du contrôle. Dans tous les cas, la stabilité du degré de blancheur fut améliorée par la subtitution du carbonate de soude et dans quelques cas, les échantillons avec le remplacement par le carbonate de soude ont produit des degrés de blancheur plus élevés aprés réversion que ceux obtenus de l'échantillon de contrôle avec la soude caustique. Un modéle mathématique fut développé afin de décrire le blanchiment au péroxyde d'hydrogéne avec la soude caustique et le carbonate de soude comme sources d'alcali. Des formettes furent fabriquées à partir d'échantillons sélectionnés de pâte. Les indices de déchirement et d'éclatement ne subirent aucun changement suite à la substitution au carbonate de soude. L'indice de rupture fut réduit de 5 à 15%.

INTRODUCTION

Peroxide bleaching of high-yield pulps has traditionally been conducted under alkaline conditions using a mixture of sodium hydroxide and sodium silicate to raise the pH and activate peroxide and lignin for effective bleaching.[1,2] Recent increases in the price and concerns over the continued availability of caustic have lead to a renewed interest in alternative sources of alkali for peroxide bleaching.

It is well-known that for a given pulp and peroxide charge, there is an optimum alkali charge that will produce the highest achievable brightness gain.[2,3] At charges below optimum, the bleaching process is slow, and there is insufficient alkali to drive the peroxide bleach reactions to completion. A high alkali charge increases the rate of the peroxide decomposition reactions, giving poor peroxide utilization. Furthermore, in a process with a fixed retention time, too much caustic leads to complete consumption of peroxide and an increase in alkaline reactions that reduce brightness.[1,4]

Silicate performs a dual role in the process as a peroxide stabilizer and as an alkaline buffer.[1,5] Adding caustic at the end of a conventional peroxide bleach stage can make use of the residual peroxide for additional brightness gains.[6] This suggests that there may be benefits in increasing the buffering capacity in the peroxide bleach process beyond that commonly obtained with silicate.

Sodium carbonate is recognized throughout the chemical industry as an alternative source of alkali for many processes. It has attracted attention in the paper industry for applications in refiner bleaching[7] and as a replacement for sodium hydroxide in oxygen bleaching[8], alkaline extraction[9], and as a sodium source in the kraft and sulfite pulping processes. Recently, it has been examined as an alkali source in peroxide bleaching of TMP.[10] The present research has investigated the efficiency of sodium carbonate as a partial replacement for caustic in peroxide bleaching of CTMP. The effects of the sodium carbonate substitution on development of pulp strength in peroxide bleaching and on the brightness stability of the bleached pulps are also reported.

RESULTS AND DISCUSSION

A commercial spruce CTMP was pretreated with 0.2% DTPA and dewatered to 25% consistency in preparation for peroxide bleaching. A series of conventional hydrogen peroxide bleaching experiments was conducted to determine the effect of the sodium hydroxide charge on final brightness. Once the caustic charge required to maximize brightness had been identified, it was reduced by 50% and 80% and sodium carbonate added to determine the brightness response with the mixed alkali. Summary results are reported in Table I. Complete experimental results are listed in Table IV and Table V following the report.

In both the 2% and 4% peroxide cases, replacement of 50% of the ideal sodium hydroxide charge with sodium carbonate results in a loss of approximately 1 point in brightness. Replacement of 80% of the caustic increases the brightness loss to 1.5 points.

A mathematical model was developed to predict brightness gain. Using a parameter fitting approach, coefficients were determined to fit the data to an equation for a parabola. The resulting equation is listed below.

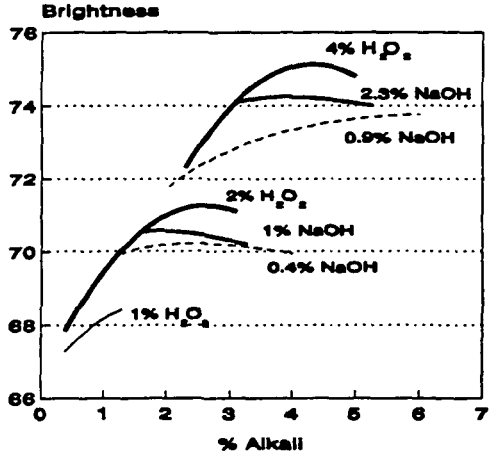

Figure 1. Model results for soda ash substitution. Alkali is the sum of the sodium hydroxide and sodium carbonate charges and does not include silicate. Starting brightness is 61 GE.

This equation has been used to prepare the summary plot in Figure 1 and the contour plots of brightness gain for the 4% (Figure 2) and 2% (Figure 3) hydrogen peroxide cases. Figure 1 demonstrates the reduced sensitivity of the bleaching response to alkali charge when sodium carbonate is used to replace some of the sodium hydroxide normally used in peroxide bleaching.

When using 4% peroxide, the maximum brightness gain is 14.5 points GE, obtained with 4.4% sodium hydroxide on OD pulp (Figure 2). The maximum brightness is obtained with sodium hydroxide as the only source of alkali. Under alkali deficient conditions, i.e., 2% sodium hydroxide charge, the initial effect of adding sodium carbonate is to fortify the alkali charge and increase the brightness gain, in this case from ≈ 11 points to 13 points GE. The slopes of the *iso*brightness lines represent the soda ash to caustic substitution ratios. In the alkali deficient region, this is about 1.8 parts carbonate to replace 1 part caustic. In the excess caustic region, the replacement ratio is quite variable, ranging from 0.7 to 1 in the high brightness gain region to ≈ 3 to 1 carbonate to caustic for the 10 point *iso*brightness line.

$$BRIGHTNESS = 61.1 + 6.56(H_2O_2)^{0.42} - 0.5(0.6 + H_2O_2 - 1.18NaOH - 1.6\sqrt{Na_2CO_3})^2 + 0.57NaOH + 0.08Na_2CO_3$$

$$R^2 = 0.94,\ SE = 0.87$$

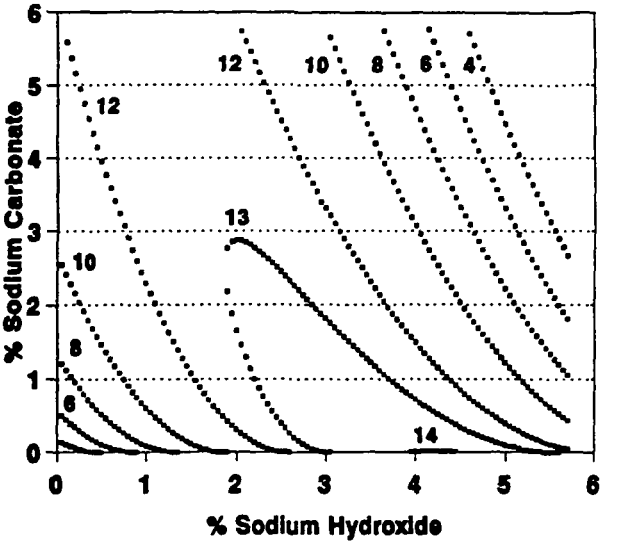

Figure 2. Contours of constant estimated brightness gain when using 4% peroxide and mixtures of sodium hydroxide and sodium carbonate.

The brightness gain contour plot for 2% peroxide (Figure 3) is very similar. Maximum brightness is achieved with the addition of 2.5% sodium hydroxide as the source of alkali. In the caustic deficient region, sodium carbonate increases brightness gain with a substitution ratio of approximately 1 to 1. In the excess alkali region, added carbonate decreases brightness with a substitution ratio, ranging from 0.5 to 1 to 2 to 1.

Evaluation of Residuals

Peroxide and alkali residuals are listed in Tables IV and V. For the caustic control cases, the alkali charge required to maximize brightness is slightly lower at the longer retention times. At maximum brightness, the final pH is lower, the strong base residual smaller, and the peroxide residual 20% larger when using sodium carbonate to supplement the caustic charge. In both the caustic and soda ash cases, the residual peroxide decreases linearly with increasing total alkali charge. The high peroxide residual in the carbonate substitution cases might be effectively utilized in a two-stage peroxide bleaching process that either recycles the residual peroxide to the first stage or reactivates the residual peroxide with a

Table I. Alkali charges at maximum brightness for the 90-minute retention time.

H_2O_2 %	NaOH %	Na_2CO_3 %	Brightness GE
2.0	2.5	-	71.8
2.0	1.0	1.3	70.6
2.0	0.4	3.2	70.3
4.0	4.0	-	75.6
4.0	2.3	1.3	74.8
4.0	0.9	4.9	74.2

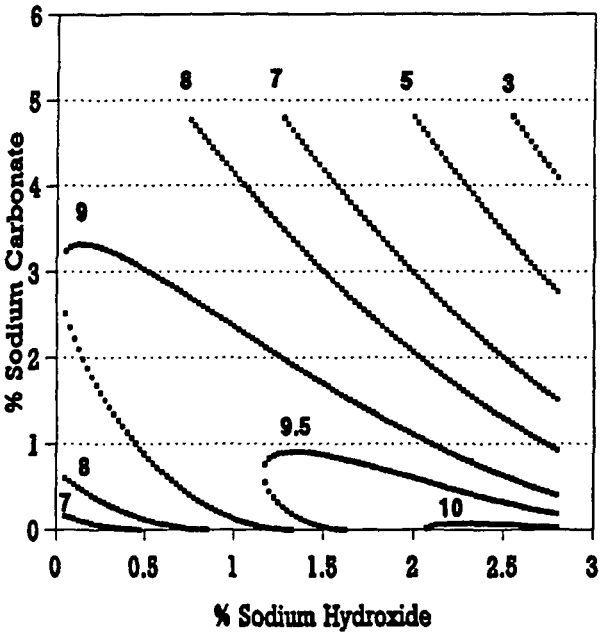

Figure 3. Contours of constant brightness gain using 2% peroxide and mixtures of sodium hydroxide and sodium carbonate.

second charge of alkali as proposed by Lachenal.[6]

Handsheet and Physical Properties

Selected samples at or near the optimum alkali charge were made into handsheets and tested for tensile, tear, and burst strength. Results of these tests are reported in Table II. There is a slight loss in tensile index when substituting carbonate for sodium hydroxide as the bleaching alkali. This is most pronounced at the 2% hydrogen peroxide level where the tensile index has been reduced by 15%. At 4% hydrogen peroxide on pulp, the loss is only about 5%. Tear index and burst index are not significantly affected by the change in alkali.

Table II. Handsheet test results on spruce CTMP bleached with hydrogen peroxide and sodium hydroxide and sodium carbonate as alkali. Results are for samples at or near the optimum alkali charge.

H_2O_2 %	NaOH %	Na_2CO_3 %	Tensile Index N·m/g	Tear Index $mN·m^2/g$	Burst Index $kPa·m^2/g$
2.0	2.5	-	17.5	6.3	0.66
2.0	1.0	1.3	15.2	5.9	0.66
2.0	0.4	3.2	15.1	5.8	0.63
4.0	4.0	-	20.2	7.6	0.88
4.0	2.3	3.0	19.2	7.8	0.84
4.0	0.94	4.9	19.7	7.6	0.83

The loss in tensile index in the samples bleached with sodium carbonate as alkali is probably a result of reduced alkaline swelling and formation of fewer carboxylic acid functional groups with the milder alkali.[11] The more pronounced effect on tensile strength at 2% than at 4% peroxide has been observed by Moldenius.[12] The relative insensitivity of tear strength to peroxide and alkali is also reported by Moldenius.

Brightness Reversion

Reverted brightness was measured on several handsheets after six and nine months of storage in an office environment. During the majority of this time, the samples were in a file drawer shielded from light. After nine months of storage, the samples were exposed to 1 hour of intense light in an Oriel Solar Simulator. Reverted brightness results are reported in Table III.

Average brightness loss after nine months storage is 2.2 points for the samples bleached with a mixture of sodium carbonate and sodium hydroxide. This compares to an average brightness loss of 4.5 points for the samples bleached with 100% sodium hydroxide. After reversion, the samples bleached with 2% peroxide and mixed alkali exceed the brightness of the sodium hydroxide control.

At the 4% peroxide bleach level, the brightness difference between the sodium hydroxide control and samples with carbonate substitution has narrowed from the original 2.5 points GE to about 1.5 points GE after reversion.

The brightness loss results appear to be sensitive to the carbonate substitution level, averaging 12.6 points loss with 100% sodium hydroxide, 11.3 points loss at 50%

Table III. Initial brightness and ambient and light reverted brightness results for samples bleached at optimum alkali charge. The 4% peroxide data is for bleaches conducted with a 3-hour retention time.

NaOH %	Na_2CO_3 %	Brightness			
		Initial	6 mo. (dark)	9 mo. (dark)	Light reverted
	2% H_2O_2				
22.5.0	-	72.6	67.6	66.8	60.2
2.01.0	1.32	71.4	70.5	69.4	61.3
2.00.4	/3.2	70.2	68.8	68.0	60.5
	4% H_2O_2				
4.04.0	-	77.5	75.1	74.3	64.7
4.02.3	3.0	75.2	73.8	72.9	62.6
4.00.9	7.4	74.1	72.7	71.8	63.6

carbonate substitution, and 10.1 points loss at 80% carbonate substitution.

The susceptibility to reversion may be dependent on the final pH of the bleach solution. *Ortho*-quinones have been detected in light reverted mechanical pulps, and the catechol, *ortho*-quinone redox couple is implicated as a major contributor to brightness reversion in high-yield pulps.[13] Hydroquinones are stable to peroxide under some bleaching conditions and, in fact, can be synthesized by the peroxide oxidation of acetoguaiacol and other suitable α-ketone precursors in the Dakin reaction.[14]

The stability of the hydroquinone may depend on the final pH. Above pH 10, hydroquinones and catechols are detected[15] as products of model compound oxidations with hydrogen peroxide. At pH 9, they readily react with peroxide,[16] and they are rarely observed as products of model compound experiments conducted at low pH or without excess caustic. Hocking has recorded the effect of different sources of alkali on conversion of *p*-hydroxyacetophenone to hydroquinone.[17] Under conditions that give a final pH under 10, Hocking observes a lower yield of hydroquinone relative to the amount of *p*-hydroxyacetophenone consumed in the reaction, consistent with an increase in decomposition of the hydroquinone.

The failure to maintain brightness when adding sodium carbonate is not fully understood. It is clear that the weaker base and buffering effect of sodium carbonate changes the pH profile of the conventional peroxide bleach. It may be that a higher initial pH obtained with sodium hydroxide promotes reactions between lignin and peroxide that are slow at the lower starting pH expected with sodium carbonate. It has also been shown that peroxide bleach efficiency is sensitive to the rate of decline in pH, as well as, the starting pH.[4] It is not possible to rule out these effects without additional experiments using other buffers.

Catechol oxidation to *o*-quinones at low residual pH adds another plausible explanation. Quinones react readily in alkali to give colored condensation products that are difficult to remove by further bleaching.[7b] If the lower final pH of the sodium carbonate experiments results in increased oxidation of catechols to *o*-quinones, the resulting condensation products could lead to a lower final brightness, while the reduction in catechols should improve the brightness stability as observed in these experiments.

A fourth possibility is a change in peroxide reactivity due to the formation of an addition complex between peroxide and carbonate. Although sodium carbonate peroxyhydrates are well-known, they hydrolyse rapidly, and the reactivity generally follows that of hydrogen peroxide.[18] However, formation of peroxycarbonates will reduce the effective concentration of hydrogen peroxide and the peroxy anion. This would result in a slower reaction rate and slower bleaching. The change in optimum pH can be either a pH sensitivity in the equilibrium for formation of the peroxycarbonate or participation of peroxycarbonate in bleaching at the lower pH. Since the optimum pH for bleaching high-yield pulps with peroxyacetic acid is around pH 8.5[19], the second of the two is a distinct possibility. It is also possible that the carbonate anion stabilizes the free radicals implicated in peroxide bleaching.[20]

Several follow-up experiments were carried out in an attempt to evaluate some of these hypotheses. Split alkali addition with sodium hydroxide added with the peroxide and sodium carbonate added 30 minutes later failed to increase the brightness to the caustic control levels. Decreasing the silicate charge by 50% or increasing the temperature to 70° C also failed to increase the brightness gain.

CONCLUSIONS

Based on the experimental work and the preceding discussions, the following conclusions can be drawn:

Sodium carbonate can be successfully substituted for up to 80% of the sodium hydroxide required in peroxide bleaching of spruce CTMP. Although the optimum ratio for replacing sodium hydroxide with sodium carbonate is sensitive to the pulp, bleaching conditions, and peroxide charge, it generally appears to be close to a normalized basis, i.e., 1.3 g of soda ash to each gram of caustic.

Sodium carbonate added as a partial replacement

for the caustic normally used in peroxide bleaching decreases the sensitivity of the bleaching process to the alkali charge and may improve control of the final brightness.

Use of sodium carbonate to replace part of the caustic required in peroxide bleaching will result in a slight loss in brightness gain, on the order of 1 to 1.5 points in TAPPI brightness.

Spruce CTMP bleached with sodium carbonate as part of the alkali charge exhibits improved brightness stability relative to conventionally bleached pulps using sodium hydroxide and sodium silicate as the only sources of alkali.

Peroxide bleaching with mixtures of sodium hydroxide and sodium carbonate results in a 5 to 15% loss in tensile strength relative to controls bleached using 100% caustic.

There is no significant change in either tear index or burst index when using sodium carbonate to replace up to 80% of the caustic requirements in peroxide bleaching.

Experimental Procedures

Hydrogen peroxide (30-35% Fisher technical grade) was diluted with distilled water to ≈ 5% peroxide and titrated periodically to determine strength. Sodium hydroxide (Mallinckrodt analytical grade anhydrous pellets) was dissolved in distilled water to a nominal solution strength of 10%, with actual strength determined by titration. Sodium silicate (Fisher Technical Grade 40 to 42 Bé), Magnesium sulfate heptahydrate (Mallinckrodt analytical reagent) and Diethylenetriamine-pentaaceticacid (DTPA) (Aldrich Chemical Company, *penta*acid form) were used as is.

A large sample of unbleached spruce CTMP was obtained from a mill in Canada and stored at 5° C until needed. Before bleaching, samples were diluted to 4% consistency and treated with 0.2% DTPA at 50° C for 30 minutes. The samples were then dewatered on a büchner funnel and centrifuged to 25% consistency or higher. The batches were recombined and blended to provide a uniform starting pulp for the experiments. A bleach liquor consisting of 3% (1.5 g) sodium silicate, 0.05% (0.025 g) magnesium sulfate (anhydrous basis), and appropriate amounts of sodium hydroxide and sodium carbonate were mixed in enough distilled water to reduce a 50 OD gram sample[21] of pulp to 20% consistency. After everything dissolved, the desired amount of hydrogen peroxide was added to the bleach liquor and the entire solution mixed with pulp in a Hobart® mixer. The sample was stirred for 10 minutes, transferred to a plastic bag, sealed, and placed in a water bath set at 60° C.

The bag remained in the constant temperature water bath for 90 minutes at which time it was opened and a filtrate sample obtained and titrated for residual peroxide[22], sodium hydroxide, sodium carbonate (pH 8.3), and sodium bicarbonate (pH 3.8).[23] The residual alkali generally behaved in titration as a mixture of sodium carbonate and sodium bicarbonate (i.e., the molar concentration of base in the pH 8.8 to pH 3.8 part of the titration exceeded the molar concentration of base in the first part of the titration). To conform with standard practice, the residual hydroxide and carbonate are reported as sodium hydroxide % on OD pulp rather than the analytically correct sodium carbonate. The bicarbonate is reported as sodium bicarbonate % on OD pulp.

The pulp was neutralized to pH ≈ 7 and handsheets formed for brightness testing (TAPPI T-218 and T-452). In some experiments using 4% peroxide, samples were taken for brightness determination at both 90 minutes and 3 hours retention times to determine if the longer retention period favored carbonate addition. Where this information is available, it is reported in Table 5. Near the end of the study, the sample size was reduced to 25g OD to conserve pulp. With the smaller sample size, it was not possible to obtain the chemical residuals on both the 90-minute and 3-hour samples. In these cases the 3-hour data was collected, and the 90-minute data is not available.

Starting pulp was sampled four times during the course of the experiments. The brightness varied from a low of 60.7 to a high of 62.0, and the changes were not correlated with time. Of the 49 data records listed, 11 are replicates (including the four unbleached controls). Average deviation from the mean for all replicated data is ±0.34 points GE brightness, with a standard deviation of 0.45.

Ambient brightness reversion was evaluated by placing the samples in plastic bags and loading them into a standard 10" X 13" interoffice envelope. The envelope was then placed in a file drawer for storage. Brightness was tested after six months and nine months of storage.

Light reverted brightness measurements were conducted on the nine-month reverted samples. The brightness tabs cut from the handsheets were clamped at a distance of 10.5" from the lens of an Oriel 1000 Watt Solar Simulator. The Solar Simulator uses a Xenon arc lamp to simulate the solar spectrum and was fitted with an air mass 1.5 global filter to model the average wavelength distribution of solar irradiation in the continental United States. An exhaust fan provided air circulation to minimize heating of the sample. Each sample was exposed for one hour. Samples were then stored for 24 hours to allow the brightness to stabilize[24] before submitting for the brightness measurement.

Regression analysis and model development were carried out using Statistical Graphics Corporation Statgraphics® 3.0.

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Table IV. Results of 90-Minute Bleaching Experiments

EXP#	H_2O_2 %	NaOH %	Na_2CO_3 %	Brightness 90 min.	Residuals, % on Pulp			pH off
					H_2O_2	NaOH	$NaHCO_3$	
38.5	0	0	0	62.0	0	0	0	7
30.5	0	0	0	61.1	0	0	0	7
0.5	0	0	0	61.1	0	0	0	7
9.5	0	0	0	60.7	0	0	0	7
1	1.0	0.8	0	67.4	0.26	0.01	1.51	8.9
2	1.0	1.1	0	68.0	0.14	0.03	1.12	9.4
3	1.0	1.3	0	67.5	0.14	0.04	1.78	9.4
4	2.0	1.5	0	70.9	0.61	0.10	2.05	9.3
5	2.0	1.75	0	71.0	0.58	0.07	2.24	9.4
13	2.0	1.75	0	70.4	0.65	0.38	2.63	9.7
20	2.0	2.0	0	71.8	0.60	0.16	2.57	9.6
6	2.0	2.0	0	71.5	0.50	0.11	2.08	9.7
11	2.0	2.0	0	70.6	0.55	0.46	2.48	9.8
18	2.0	2.25	0	71.2	0.62	0.37	2.25	9.9
27	2.0	2.5	0	71.8	0.62	0.52	2.11	10.1
21	2.0	2.5	0	72.6	0.56	0.41	2.32	9.9
28	2.0	3.0	0	70.6	0.54	0.77	1.63	10.4
39	2.0	1.0	0.75	69.9	0.86	0.13	3.96	9.3
24	2.0	1.0	1.0	70.4	0.79	0.07	3.02	9.0
26	2.0	1.0	1.32	71.4	0.72	0.16	3.26	8.6
16	2.0	1.0	1.32	69.9	0.61	0.30	2.69	9.4
22	2.0	1.0	1.32	70.6	0.62	0.11	3.29	9.0
12	2.0	1.0	2.0	69.4	0.58	0.57	3.53	9.5
14	2.0	1.0	3.0	69.2	0.49	0.87	3.59	9.8
40	2.0	1.0	4.5	70.1	0.65	0.96	4.86	9.7
23	2.0	0.4	1.5	70.0	0.81	0.04	2.99	8.8
15	2.0	0.4	2.12	70.1	0.71	0.27	3.26	9.2
17	2.0	0.4	3.2	70.4	0.61	0.27	4.32	9.2
25	2.0	0.4	3.2	70.2	0.72	0.23	4.59	9.1
19	2.0	0.4	4.24	69.6	0.66	0.32	4.68	9.3
10	2.0	0.4	4.24	68.6	0.50	0.95	4.05	9.7
41	2.0	0.4	6.25	70.4	0.59	0.96	5.5	9.6
7	4.0	2.8	0	73.7	0.69	0.14	0.91	10.4
8	4.0	3.1	0	74.5	2.08	0.79	1.99	10.5
30	4.0	3.4	0	74.8	1.96	0.47	2.42	10.0
9	4.0	3.4	0	74.8	1.89	0.84	2.60	10.5
29	4.0	4.0	0	75.6	1.45	1.12	1.57	N.A.
31	4.0	4.6	0	77.2	1.71	1.65	0.66	10.9
32	4.0	5.2	0	72.8	N.A.	N.A.	N.A.	N.A.
43	4.0	2.3	1.3	74.8	N.A.	N.A.	N.A.	9.7
33	4.0	2.3	3.05	74.2	1.98	N.A.	N.A.	9.9
34	4.0	2.3	4.6	70.8	N.A.	N.A.	N.A.	N.A.
35	4.0	2.3	6.1	71.4	N.A.	N.A.	N.A.	N.A.
42	4.0	2.3	8.2	71.1	N.A.	N.A.	N.A.	N.A.
45	4.0	0.92	1.54	72.8	N.A.	N.A.	N.A.	8.8
36	4.0	0.92	4.88	74.2	N.A.	N.A.	N.A.	9.5
37	4.0	0.92	7.36	74.0	N.A.	N.A.	N.A.	9.6
38	4.0	0.92	9.75	71.3	N.A.	N.A.	N.A.	N.A.
44	4.0	0.92	12.8	73.4	N.A.	N.A.	N.A.	9.9

Table V. Peroxide Bleaching Data for 3-Hour Retention Times

EXP#	H2O2 %	NaOH %	Na2CO3 %	Brightness 3 Hours	Residuals, % on Pulp			pH off
					H_2O_2	NaOH	$NaHCO_3$	
0	0	0	0	61.1	0	0	0	7
9.5	0	0	0	60.7	0	0	0	7
30.5	0	0	0	61.1	0	0	0	7
38.5	0	0	0	62.0	0	0	0	7
30	4.0	3.4	0	76.9	2.00	0.46	2.9	9.8
29	4.0	4.0	0	77.5	1.45	1.12	1.57	10.5
31	4.0	4.6	0	77.8	1.37	1.57	1.27	10.9
32	4.0	5.2	0	75.4	1.17	1.55	0.69	11.1
43	4.0	2.3	1.3	76.1	1.85	0.5	3.77	9.5
33	4.0	2.3	3.05	75.2	1.66	0.88	4.1	9.6
34	4.0	2.3	4.6	72.6	1.54	1.39	4.56	9.8
35	4.0	2.3	6.1	73.9	1.43	1.83	5.04	9.8
42	4.0	2.3	8.2	73.2	0.78	4.04	2.2	10.9
45	4.0	0.92	1.54	74.6	2.09	0.11	3.29	9.0
36	4.0	0.92	4.88	74.7	1.62	0.54	5.97	9.3
37	4.0	0.92	7.36	74.1	1.22	1.18	6.76	9.5
38	4.0	0.92	9.75	73.3	1.01	1.89	7.13	9.7
44	4.0	0.92	12.8	74.9	1.07	2.83	8.18	9.6